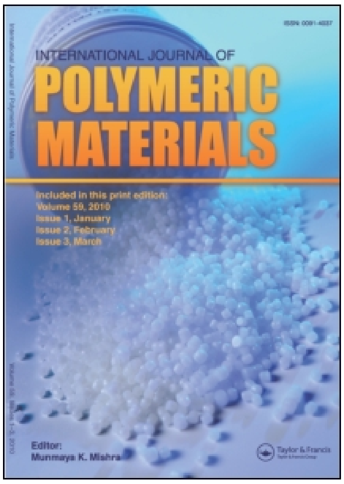

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The Effects of Network Imperfections on the Small-Strain Moduli of Polydimethylsiloxane Elastomers Having High Functionality Cross Links

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The Effects of Network Imperfections on the Small-Strain Moduli of Polydimethylsiloxane Elastomers Having High Functionality Cross Links

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Poly(dimethylsiloxane) networks of high cross-link functionality have been prepared by end linking vinyl-terminated chains with multifunctional poly(methylhydrosiloxane) chains. They covered a wide range in the extent of reaction, P_{vi}, of the vinyl end groups. At small strains, these networks had elongation moduli that significantly exceeded the values predicted by the Flory-Erman theory. Neglected in such standard analyses, however, is the fact that the segments between cross links along the junction precursor molecule can themselves act as short network chains, contributing to the modulus and giving a strongly bimodal distribution of both network chain lengths and cross-link functionalities. As would be expected, an unmistakable transition is observed in values of the shear modulus G toward the phantom limit of deformation as the crosslink density increases. Calculations based on recognition of such short chains give results in much better agreement with experiment. The results so obtained showed strong dependence of the elastomeric properties on the extents of reaction and the inherent network imperfections. Such imperfections have a pronounced effect on the equilibrium modulus, more specifically on the empirical constant $2C_2$. The dependence of $2C_2$ on the volume fraction of the elastically "effective" chains is thus established. Moreover, the results unambiguously demonstrate that the empirical constant $2C_2$ is essentially a topological contribution and contains no contributions from the chemical network.

KEY WORDS Network, imperfections, polydimethylsiloxane, modulus, elastomers.

INTRODUCTION

Silicone networks of high junction functionality are prepared by end linking vinyl-terminated groups on the α, ω modification of poly(dimethylsiloxane) (PDMS) with Si-H groups in the junction precursor poly(hydromethylsiloxane) $[\text{—SiH(CH}_3\text{)O—}]_x$. Such networks have been prepared and their elastomeric properties have been reported in the literature.[1-7] They have been formed under conditions of varying molar ratio R of Si-H groups to vinyl end groups. Networks with

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high extent of reaction of vinyl groups ($P_{vi} > 0.9$) were prepared by having R slightly greater than unity (i.e., excess Si-H groups). In one of these studies,[5] networks were formed such that P_{vi} covered a wide range of values, from 0.40 to 0.95. This was achieved by having $R < 1$, and under such conditions the end-linking reaction does not go to completion.

The most interesting result obtained in these studies is the observation that the shear moduli in the small deformation limit considerably exceeded the values predicted from the expected junction functionality ϕ and the concentration of elastically effective chains expected from the stoichiometry of the end-linking reaction.[1-7] Another interesting observation concerns the dependence of the fluctuations of the junctions on their functionality. The modulus or reduced stress $[f^*]$ is commonly defined as[8-11]

$$[f^*] = fv_2^{1/3}/A^*(\alpha - \alpha^{-2}) \tag{1}$$

where f is the equilibrium elastic force, A^* the cross-sectional area of the undeformed sample, α the elongation or relative length of the sample, and with v_2 being the volume fraction of polymer during the stress-strain measurements.

The dependence of the reduced stress on the elongation α is generally represented by the semi-empirical, Mooney-Rivlin Equation[9-12]

$$[f^*] = 2C_1 + 2C_2\alpha^{-1} \tag{2}$$

where $2C_1$ and $2C_2$ are constants independent of α. The constant $2C_1$ is thought to approximate the modulus in the high-elongation limit of an idealized "phantom" network, where the network junctions undergo very large fluctuations.[10,13-19] The constant $G \approx 2C_1 + 2C_2$ then approximates the modulus in the limit of very small deformations, where chain-junction entangling suppresses the fluctuations, causing the network chain dimensions to change affinely (linearly) with changes in the macroscopic dimensions of the sample.[8-10] The constant $2C_2$ is then viewed as representing the decrease in modulus resulting from the deformation becoming increasingly non-affine as the elongation increases.[10,19] The junction fluctuations that cause this non-affineness should be suppressed when the cross-link functionality is high, because of the larger number of chains emanating from such cross links.[10,15-19] Thus, $2C_2$ is predicted to be very small and would asymptotically approach zero with increase in ϕ.[10,15-19] The reported values of $2C_2$, however, were relatively large, even for $\phi > 30$.[2-7]

Recently, attention has been focused on the short chain segments between the cross-linking points along the junction precursor molecules.[20-23] Such segments were found, inadvertently, to act as short network chains, thus contributing to the modulus and giving a strongly bimodal distribution of both network chain lengths and cross-link functionalities. Reexamination of some of the published results on this basis for networks that covered a range in the extent of reaction of vinyl groups gave much better agreement between experiment and theory.[20-23] More specifically, consideration of the possibly bimodal nature of these high-functionality networks provided a reasonable explanation of their unexpectedly high values of the phantom modulus $2C_1$.[20-23] This revised interpretation also explained the observations that the empirical constant $2C_2$ was not as small as expected.[20-23] Small values of $2C_2$ would have required that junction fluctuations be suppressed at all elongation, and this is not true for the short chains because of their being attached to junctions of low functionality and because of their reduced interpenetration. Additional complications in networks which intentionally prepared so as to cover a wide range of extent of reaction, specifically $P_{vi} \sim 0.40 - 0.95$, were also treated by resorting to the same model. More specifically, the extent of reaction should affect the numbers and lengths of the short chains introduced from the end-linking molecules, and also the effective functionalities they impose on the long network chains themselves.[20-23]

It should be noted that in most of the relevant experimental studies,[2-6] attention was focused only on the small-strain modulus. Pertinent here is the fact that values of the empirical constant $2C_2$ were found to depend on the extent of reaction. At lower extents of reaction, numerous network imperfections, particularly, dangling ends are expected to be present, and thus would act as a diluent even in the dry unswollen state. As is well known, the constant $2C_2$ and the related ratio $2C_2/2C_1$ decrease with swelling. Very little quantitative information is known, however, about the dependence of elastomeric properties, particularly $2C_2$, on the network imperfections. The present paper therefore reexamines the small strain results, in order to scrutinize contributions to the modulus from such imperfections, in general.

STRUCTURAL CONSIDERATIONS AND THE THEORY OF ELASTICITY

In the case of a silane end-linking agent having very high functionality, sequences between the Si-H groups that have reacted (i.e., between cross links) could well be of sufficient length to act as network chains themselves, yielding a bimodal network.[20-23] Some of the largest improvements in properties of networks intentionally made to be bimodal occur, in fact, when the short chains have only six skeletal bonds, the minimum number investigated to date.[24,25] The length for maximum effect could thus even be smaller.[24,25]

Such short chains would effectively be cross-linked with trifunctional junctions, as illustrated in Figure 1(a).[21,22] The long chains, on the other hand, would then effectively be cross-linked by junctions of lower functionality than would be suggested by the functionality of the silane itself. As can be seen from part (b) of the sketch, introducing a new long chain (shown dashed) increases the number of short chains by two. Thus, each long chain (l) would give rise to two short chains (s).[21,22]

Molecular theories of rubberlike elasticity can be divided into two categories: those based on networks which deform affinely (linearly) with the macroscopic deformation, and those based on phantom networks.[10] Both theories are based on simple Gaussian statistics of the network-chain end-to-end distances. In an affine network, fluctuations of the junctions are suppressed by neighboring chains sharing the same region of space.[10] Consequently, the chain junctions undergo affine displacements, and the reduced stress for a perfect network is given by[8-10]

$$[f^*]_{\mathrm{aff}} = \nu RT(V/V_0)^{2/3} \tag{3}$$

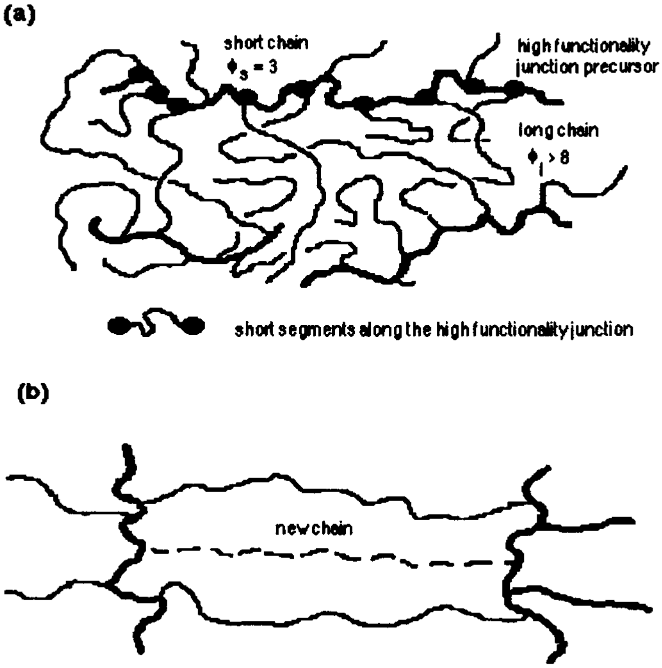

FIGURE 1 Sketches showing parts of a network having high-functionality cross links. Part (a) shows how segments between cross links along the end-linker molecule (darkened chains) can act as short chains in a bimodal network. Part (b) demonstrates the two-to-one correspondence of short chains thus generated to the long chains giving rise to them.[21,22]

where ν is the number density of elastically effective chains (joined to junctions of functionality $\phi \geq 2$),[19] R the gas constant, T the absolute temperature, V the volume of the network, and V_0 the reference volume (at which the network was prepared).

In the phantom network, on the other hand, the chains are assumed to be devoid of material properties, i.e., they can move freely through one another.[10,15–19] The mean positions of the junctions are affine in the strain, but the fluctuations about the mean positions are invariant with strain. The modulus is expressed as[10,15–19]

$$[f^*]_{ph} = \xi RT(V/V_0)^{2/3} \tag{4}$$

where

$$\xi = \nu_a - \mu_a = \nu - \mu \tag{5}$$

is the cycle rank of the network, ν_a and μ_a are the number density of elastically active chains and junctions, respectively, and μ is the number density of the elastically effective junctions. For a perfect network having functionality ϕ, the cycle rank is expressed as[19]

$$\xi = \left(1 - \frac{2}{\phi}\right) \nu_a \tag{6}$$

The number of active junctions μ_a is given by[19]

$$\mu_a = (2/\phi)\nu_a = [2/(\phi - 2)]\xi \tag{7}$$

In simple elongation of real networks, the stress-strain isotherm lies between these two limits.[10,15–19] The Flory-Erman theory[15–18] assume that the fluctuations of the junctions about their mean positions are constrained by interactions with neighboring chains. According to this theory, the reduced stress is given by[15–18]

$$[f^*] = [f^*]_{ph} + [f^*]_c = [f^*]_{ph}(1 + f_c/f_{ph}) \tag{8}$$

where f_c and $[f^*]_c$ are the force and reduced force arising from the constraints on the fluctuations, and f_{ph} and $[f^*]_{ph}$ are the corresponding quantities predicted from the phantom network theory. The ratio f_c/f_{ph} is strain dependent and depends on two parameters, namely κ and ζ.[15–18] The more important of the two is κ which serves as a measure of the severity of the entanglement constraints relative to those in a phantom network.[15–18] The other parameter is ζ which takes into account the possibly non-affine transformations of the domains of constraints with increasing deformation.[15–18] These quantities and the underlying theory are discussed in greater details elsewhere. The theory predicts that f_c/f_{ph} vanishes in the limit of high deformation. Hence, the modulus would approach the phantom limit at $\alpha \to \infty$. It should also vanish as the functionality of the network increases.[15–18] The relative contribution from the constraints specifically in the affine limit ($\alpha \to 1$, $\kappa \to \infty$) is predicted to be[15–18]

$$f_c/f_{ph} = 2/(\phi - 2) \tag{9}$$

Previous results on PDMS networks indicate that κ is related to the phantom modulus, and consequently to the phenomenological parameter $2C_1$.[26] It has been possible to estimate values of the parameter κ for such bimodal networks, according to the relationship[21]

$$\kappa = (A/[f^*]_{ph}^{1/2})\,[(2/\phi_l) + 4/3]\,[(1 - 2/\phi_l) + 2/3]^{1/2}(2)^{3/2} \tag{10}$$

where A is a constant found to have a value of 2.0 $N^{1/2}$ mm^{-1} for model PDMS networks, according to data reported elsewhere.[26]

If the short segments along the cross-linking precursor are elastically effective as network chains then the number of new chains is equal to 2ν, having $\phi = 3$.

Thus ν increases by the factor 3. In the case of an affine network, the modulus would also increase by a factor of 3. That is

$$[f^*]_{\mathrm{aff}} = 3\nu_a RT \tag{11}$$

In the high-deformation, phantom limit, the modulus of the networks under consideration is predicted to be[21,22]

$$[f^*]_{ph} = (\nu_a - \mu_a)RT + (1 - 2/\phi_s)2\nu_a RT \tag{12}$$

where the functionality ϕ_s associated with the short chains is always three. The average functionality ϕ_l associated with the long chains is expected to be presumably large.[2–4] In any case, in the limit of very large functionality $(1 - 2/\phi_l)$ would approach unity. Consequently, we obtain[21,22]

$$[f^*]_{ph} = (5/3)\nu_a RT \tag{13}$$

Such result is at variance with topological considerations discussed above that require the preservation of the cycle rank. However, the above result is in agreement with a wealth of experimental evidence. The experiments have shown that the elastomeric properties for bimodal networks are dependent on the mole fraction of the short chains present in the network as well as the ratio of lengths of the short chains to the long ones.[19–21]

In treatments ignoring the presence of the short chains,[6] the affine and phantom moduli would simply be[1–7]

$$[f^*]_{\mathrm{aff}} = \nu_a RT \tag{14}$$

$$[f^*]_{ph} = (1 - 2/\phi_l)\nu_a RT \approx \nu_a RT \tag{15}$$

At low extents of reaction, the situation would be different in that all junctions would be effectively trifunctional ($\phi = 3$). The modulus in the phantom limit has been predicted to be[22]

$$[f^*]_{ph} = (1 - 2/\phi)3\nu_a RT = \nu_a RT \tag{16}$$

This means that the increase in the modulus from the increased number of chains is exactly offset by the decrease in functionality, and the result is the same as that obtained treating the network as a simple unimodal network with high functionality.[22]

Also it is important to underline here that the identification of ν_a with ν is proper only for perfect networks otherwise it is an approximation that is legitimate for high functionality networks. It is important to note here that, in general, $\nu \neq \nu_a$.[27]

Flory[27] has shown that the effective number of chains for an imperfect network is expressed universally by

$$\nu = 2\xi \tag{17}$$

COMPARISONS BETWEEN THEORY AND EXPERIMENT

The relevant published experimental results[1-7] are now analyzed on the basis of the revised model discussed above. The extents of reaction, the number of elastically effective chains, effective functionality, and other structural parameters of the network are derived by the branching theory.[2-6] The resutls are tabulated in Table I. The experimental moduli at small strains have been obtained from a Mooney-Rivlin fit. The straight lines obtained can be extrapolated to zero deformation ($\alpha^{-1} = 1$) and the value of the reduced force is then $2C_1 + 2C_2$ which is generally associated with the shear modulus G at small deformation.[1-7,19] This method is known to overestimate the value of G by about 5%.[6,19] Such a difference should be tolerable for the present purpose. As has been already mentioned, the constant $2C_2$ is a measure of the change in the reduced force for the transition between the two extremes of deformation and should approach zero for networks having high cross-link functionalities.[6,15-19] In the affine network fluctuations of the junctions are totally suppressed.[10,15-19] According to the constrained junction theory, the affine modulus $[f^*]_{\mathrm{aff}}$ of real networks, is between the affine and phantom limits even in the isotropic undeformed state.[10,15-19]

In Figure 2, values of G as approximated by $2C_1 + 2C_2$ are plotted against values of νRT for networks that are prepared under conditions of high extent of reaction of vinyl groups ($P_{vi} > 0.9$).[2,7] The solid line represents theory according to which the affine modulus for a bimodal network calculated according to Equation (11), where $\kappa \to \infty$. The dotted line shows values of the phantom modulus $[f^*]_{ph}$ calculated according to Equation (12). It is worthy to note here that at values of $\nu RT < 0.04\ N\ \mathrm{mm}^{-2}$ there is a lack of experimental data. The data, so presented, do not unambiguously suggest any appreciable intercept with the ordinate, within limits set by the scatter of the data. We shall see below that this seems to be true. An intercept with the ordinate has been often attributed to contributions from trapped entanglements.[2-6]

It is noteworthy here that the enhancement of $[f^*]$ at $\alpha \to 1$ has been observed to vanish upon swelling, suggesting it is due to difficulties in reaching elastic equilibrium when the network chains are very long.[19,26] Also such an enhancement could be plausibly due to higher slopes in Mooney-Rivlin fits for samples with high molecular mass M_c between crosslinks and so the extrapolation overestimates G.[19] Thus, the small-strain modulus G is expected to vanish in the limit $\nu RT \to 0$. For purposes of comparison, the dotted and dashed line represent results according to the standard unimodal representation of such networks, i.e., with total neglect of the short chains coming from the junction precursor, according to Equation (14).

The interesting point here is that at intermediate values of νRT, values of G exhibit an unmistakable transition towards the phantom limit of the modulus.

TABLE I

Elastomeric properties of high functionality polydimethylsiloxane (PDMS) networks

Source	M_n[a] g mol-1	r[b]	ω_e[c]	P_{vl}[d]	ϕ_o[e]	ϕ_e[f]	υ_2[g]	νRT[h] N mm-2	$[f^*]_u$[i] N mm-2	$2C_1$[j] N mm-2	$[f^*]_b$[k] N mm-2	$2C_2$ N mm-2	$2C_2'$[l] N mm-2
Meyers *et al.*[2]	8800	1.20	0.0000	0.961	23.8	18.3	23.8	0.254	0.227	0.390	0.396	0.087	0.102
	10100	1.20	0.0020	0.955	23.8	18.0	23.8	0.220	0.196	0.408	0.342	0.062	0.076
	11100	1.20	0.0015	0.961	23.8	18.3	23.8	0.202	0.180	0.377	0.315	0.061	0.073
	12900	1.20	0.0028	0.947	23.8	17.7	23.8	0.171	0.152	0.306	0.265	0.078	0.098
	17000	1.20	0.0027	0.948	23.8	17.9	23.8	0.130	0.116	0.232	0.202	0.097	0.118
	21600	1.21	0.0022	0.953	23.8	17.9	23.8	0.103	0.092	0.191	0.161	0.126	0.147
	25300	1.65	0.0083	0.909	23.8	11.9	23.8	0.082	0.068	0.165	0.123	0.082	0.118
	28100	1.16	0.0012	0.965	23.8	19.1	23.8	0.081	0.073	0.177	0.127	0.121	0.136
	12200	1.25	0.0018	0.957	23.8	17.4	23.8	0.183	0.162	0.325	0.284	0.078	0.093
	13900	1.65	0.0064	0.919	23.8	12.2	23.8	0.151	0.126	0.225	0.227	0.065	0.093
	14300	1.28	0.0042	0.935	23.8	16.2	23.8	0.151	0.133	0.250	0.233	0.097	0.124
	15200	1.30	0.0052	0.928	23.8	15.7	23.8	0.141	0.123	0.268	0.217	0.091	0.120
	17400	1.65	0.0053	0.927	23.8	12.4	23.8	0.123	0.103	0.200	0.185	0.056	0.079
	22000	1.31	0.0019	0.956	23.8	16.6	23.8	0.102	0.090	0.198	0.158	0.114	0.133
	27500	1.36	0.0031	0.944	23.8	15.6	23.8	0.080	0.070	0.174	0.123	0.091	0.113
	29500	1.34	0.0026	0.949	23.8	16.0	23.8	0.075	0.066	0.170	0.116	0.101	0.122
	41700	1.65	0.0088	0.906	23.8	11.8	23.8	0.050	0.041	0.129	0.075	0.101	0.142
	51000	1.42	0.0076	0.913	23.8	14.0	23.8	0.041	0.035	0.106	0.063	0.105	0.143
	52800	1.40	0.0071	0.916	23.8	14.2	23.8	0.040	0.034	0.094	0.061	0.098	0.134
	8800	1.11	0.0017	0.958	43.9	36.2	43.9	0.254	0.240	0.360	0.409	0.130	0.149
	10100	1.27	0.0017	0.958	43.9	31.8	43.9	0.221	0.207	0.373	0.354	0.078	0.093
	11100	1.20	0.0045	0.933	43.9	31.8	43.9	0.194	0.182	0.316	0.311	0.053	0.073
	12900	1.30	0.0021	0.954	43.9	30.8	43.9	0.172	0.161	0.277	0.276	0.097	0.116
	17000	1.31	0.0019	0.956	43.9	30.7	43.9	0.132	0.123	0.216	0.211	0.113	0.132
	21600	1.36	0.0038	0.938	43.9	28.4	43.9	0.101	0.094	0.180	0.161	0.104	0.130
	28100	1.45	0.0033	0.942	43.9	26.9	43.9	0.078	0.072	0.175	0.125	0.109	0.134
	12200	1.29	0.0037	0.939	43.9	29.9	43.9	0.178	0.166	0.316	0.285	0.070	0.091
	14300	1.30	0.0048	0.930	43.9	29.1	43.9	0.150	0.140	0.255	0.240	0.094	0.122
	15200	1.80	0.0069	0.916	43.9	20.4	43.9	0.138	0.124	0.212	0.216	0.127	0.166
	18300	1.80	0.0067	0.918	43.9	20.6	43.9	0.115	0.104	0.242	0.180	0.065	0.093
	22000	1.35	0.0035	0.941	43.9	28.8	43.9	0.100	0.093	0.193	0.159	0.108	0.131
	25300	1.80	0.0064	0.920	43.9	20.6	43.9	0.084	0.076	0.198	0.131	0.059	0.085
	27500	1.39	0.0042	0.935	43.9	27.6	43.9	0.079	0.073	0.173	0.126	0.101	0.128
	29500	1.40	0.0058	0.924	43.9	26.7	43.9	0.072	0.067	0.164	0.115	0.082	0.111
	52800	1.52	0.0097	0.901	43.9	23.5	43.9	0.039	0.036	0.082	0.062	0.094	0.135
	11100	1.25	0.0052	0.927	10.5	7.2	10.5	0.192	0.139	0.298	0.267	0.074	0.100
	21600	1.25	0.0049	0.930	10.5	7.3	10.5	0.100	0.072	0.180	0.139	0.101	0.131
	11100	1.39	0.0014	0.962	21.5	14.3	21.5	0.202	0.174	0.358	0.309	0.083	0.097
	21600	1.40	0.0018	0.957	21.5	14.1	21.5	0.104	0.089	0.191	0.159	0.105	0.123
	11100	1.30	0.0013	0.964	33.0	23.6	33.0	0.203	0.186	0.375	0.321	0.060	0.071
	21600	1.32	0.0036	0.940	33.0	22.1	33.0	0.101	0.092	0.186	0.160	0.102	0.127
	11100	1.22	0.0051	0.928	38.1	27.0	38.1	0.192	0.178	0.351	0.306	0.052	0.074
	21600	1.22	0.0051	0.928	38.1	27.0	38.1	0.100	0.092	0.200	0.159	0.088	0.116
	11100	1.30	0.0026	0.949	58.4	40.6	58.4	0.198	0.189	0.355	0.321	0.054	0.069
	13900	1.80	0.0095	0.902	58.4	26.4	58.4	0.147	0.135	0.253	0.233	0.075	0.112
	21600	1.37	0.0025	0.950	58.4	38.3	58.4	0.103	0.097	0.191	0.166	0.110	0.132
	11100	1.35	0.0014	0.962	83.6	57.3	83.6	0.202	0.195	0.361	0.330	0.065	0.077
	21600	1.36	0.0041	0.936	83.6	53.7	83.6	0.101	0.097	0.201	0.164	0.108	0.136
Kirk *et al.*[5]	9320	1.21	0.0009	0.970	43.9	34.3	43.9	0.243	0.229	0.435	0.391	0.098	0.110
	9320	1.12	0.0063	0.920	43.9	33.1	43.9	0.226	0.212	0.357	0.363	0.073	0.102
	9320	0.98	0.0623	0.749	43.9	25.1	43.9	0.160	0.147	0.168	0.253	0.356	0.111
	9320	0.95	0.0637	0.746	43.9	25.6	43.9	0.159	0.146	0.154	0.252	0.068	0.169
	9320	0.93	0.0822	0.711	43.9	24.0	43.9	0.145	0.133	0.162	0.229	0.032	0.116
	9320	0.86	0.1560	0.603	43.9	18.5	43.9	0.102	0.091	0.129	0.160	0.000	0.000
	11100	1.20	0.0046	0.932	43.9	31.7	43.9	0.193	0.181	0.316	0.310	0.053	0.074
	11100	1.11	0.0768	0.721	43.9	20.6	43.9	0.125	0.113	0.143	0.196	0.041	0.132
	11100	1.01	0.1390	0.625	43.9	17.0	43.9	0.093	0.082	0.109	0.144	0.000	0.000
	11100	0.98	0.1520	0.608	43.9	16.6	43.9	0.088	0.077	0.102	0.136	0.000	0.000
	11100	0.96	0.1640	0.593	43.9	16.1	43.9	0.083	0.073	0.080	0.128	0.000	0.000
	11100	0.92	0.2160	0.533	43.9	13.5	43.9	0.065	0.055	0.074	0.099	0.005	0.061
	17400	1.65	0.0052	0.928	43.9	22.9	43.9	0.123	0.112	0.200	0.194	0.056	0.079
	17400	1.15	0.0488	0.778	43.9	23.1	43.9	0.092	0.084	0.142	0.146	0.030	0.091
	17400	1.10	0.0620	0.750	43.9	22.4	43.9	0.086	0.079	0.133	0.136	0.019	0.075
	17400	1.00	0.1560	0.604	43.9	15.9	43.9	0.055	0.048	0.087	0.085	0.014	0.095
	17400	0.99	0.2020	0.549	43.9	13.3	43.9	0.045	0.038	0.064	0.068	0.019	0.119
	17400	0.93	0.1830	0.571	43.9	15.3	43.9	0.049	0.043	0.062	0.075	0.025	0.134
	17400	0.85	0.2840	0.465	43.9	11.2	43.9	0.030	0.025	0.052	0.045	0.002	0.039
	21600	1.36	0.0038	0.938	43.9	28.4	43.9	0.101	0.094	0.180	0.161	0.104	0.130
	21600	1.17	0.0829	0.711	43.9	19.0	43.9	0.063	0.056	0.094	0.098	0.020	0.089
	21600	1.05	0.1350	0.631	43.9	16.7	43.9	0.049	0.043	0.059	0.076	0.012	0.083
	21600	0.95	0.2320	0.517	43.9	12.4	43.9	0.031	0.026	0.042	0.047	0.004	0.056
	21600	0.94	0.2680	0.481	43.9	10.8	43.9	0.026	0.021	0.031	0.039	0.008	0.079
	21600	0.83	0.3580	0.400	43.9	8.5	43.9	0.016	0.013	0.023	0.023	0.000	0.000
	28100	1.45	0.0033	0.942	43.9	26.9	43.9	0.078	0.072	0.175	0.125	0.109	0.134
	28100	1.15	0.1130	0.663	43.9	16.7	43.9	0.042	0.037	0.076	0.065	0.021	0.105
	28100	1.04	0.1740	0.582	43.9	14.3	43.9	0.032	0.027	0.047	0.048	0.021	0.121
	28100	0.92	0.3310	0.424	43.9	8.5	43.9	0.015	0.011	0.033	0.021	0.003	0.045
	28100	0.88	0.3460	0.411	43.9	8.4	43.9	0.014	0.010	0.024	0.019	0.000	0.000

TABLE I (*continued*)

Source	M_n[a] g mol-1	r[b]	ω_s[c]	p_{vl}[d]	ϕ_o[e]	ϕ_e[f]	υ_2[g]	νRT[h] N mm^{-2}	$[f^*]_u$[i] N mm^{-2}	$2C_1$[j] N mm^{-2}	$[f^*]_b$[k] N mm^{-2}	$2C_2$ N mm^{-2}	$2C_2'$[l] N mm^{-2}
	28100	0.87	0.3190	0.434	43.9	9.5	43.9	0.016	0.012	0.032	0.023	0.000	0.000
Llorente and Mark[1]	11300	1.00	0.0330	0.817	11.0	7.3	11.0	0.154	0.112	0.287	0.215	0.011	0.038
	11300	1.00	0.0330	0.817	11.0	7.3	11.0	0.154	0.112	0.294	0.215	0.012	0.041
	11300	1.00	0.0610	0.752	37.0	20.9	37.0	0.133	0.120	0.232	0.209	0.007	0.040
	11300	1.00	0.0500	0.775	37.0	22.2	37.0	0.141	0.128	0.231	0.222	0.039	0.109
	11300	1.00	0.0480	0.780	37.0	22.5	37.0	0.142	0.130	0.225	0.224	0.012	0.049
Opperman and Rehage[7]	26000	1.00	0.0000	1.000	17.5	17.5	17.5	0.103	0.091	0.205	0.160	0.085	0.085
	26000	1.00	0.0000	1.000	37.5	37.5	37.5	0.103	0.097	0.211	0.166	0.108	0.108
	26000	1.00	0.0000	1.000	60.0	60.0	60.0	0.103	0.100	0.252	0.168	0.080	0.080
	26000	1.00	0.0000	1.000	75.0	75.0	75.0	0.103	0.100	0.152	0.169	0.136	0.136
	26000	1.00	0.0000	1.000	25.0	25.0	25.0	0.103	0.095	0.152	0.163	0.136	0.136
	26000	1.00	0.0000	1.000	16.5	16.5	16.5	0.101	0.089	0.198	0.156	0.076	0.076
	26000	1.00	0.0000	1.000	12.5	12.5	12.5	0.099	0.083	0.142	0.149	0.128	0.128
	26000	1.00	0.0000	1.000	10.0	10.0	10.0	0.098	0.078	0.147	0.144	0.105	0.105
	26000	1.00	0.0000	1.000	25.0	25.0	25.0	0.101	0.093	0.170	0.160	0.106	0.106
	26000	1.00	0.0000	1.000	41.0	41.0	41.0	0.101	0.096	0.144	0.163	0.116	0.116

a Number average molecular mass of α,ω–divinyl Polydimethylsiloxane
b molar ratio of Si-H groups to vinyl end groups.
c sol fraction.
d extent of reaction of the vinyl group
e initial functionality of the junction precursor.
f effective functionality of the network.
g The volume fraction of the elastically effective chains in the dry unswollen state calculated according to equation (A9) in refernce (29).
h A measure of the network chain density as obtained from the sol fraction.[6]
i Values of the phantom modulus using the usual assumption of a unimodal network, from equation (9).
k Values of the phantom modulus using the revised equation (7) which recognizes the bimodal nature of the network.
l obtained according to equation (19).

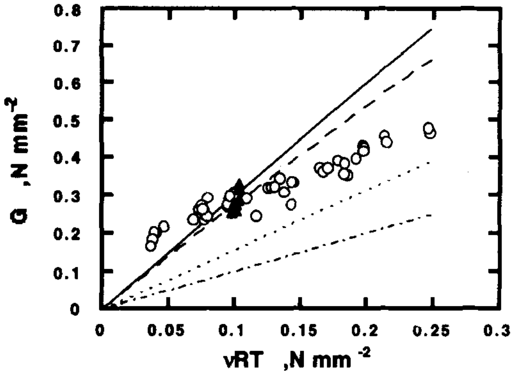

FIGURE 2 The shear modulus G for networks having high extents of reaction of the vinyl groups, as approximated by $2C_1 + 2C_2$, shown as a function of νRT (a measure of the degree of the cross-linking obtained from the end-linking chemistry).[23] The circles represent results that were obtained by Meyers *et al.*[2] and the filled triangles by Opperman and Rehage.[7] The solid line represents the results from the present calculations, which do take them into account, according to Equation (11). The dotted and dashed line represents results calculated from the unimodal representation of the networks, i.e., with total neglect of any contributions from the short chains coming from the end-linking molecules themselves, in accordance with Equation (14). The dotted line represents the results of using the new interpretation for the phantom modulus, in accordance with Equation (12). The dashed line represents the results of calculations according to the Flory–Erman theory, in accordance to Equation (8).[15–18]

Again, actual values of G predicted by the constrained junction theory should fall below the upper bound even at small strain.[19,23] Such a decrease in values of G with increase in cross-link density is expected. Such behavior is essentially due to the decrease in the degree of interpenetration and so the severity on the fluctuation of junctions, as the network chain lengths decrease.[19,23] The present analysis on the grounds of the constrained junction theory allows for a decrease in the degree of interpenetration as the network chain lengths decrease.[19,23] Intuitively, and according to theory, the modulus $[f^*]_c$ due to constraints should increase with an increase in the number of junctions μ (i.e., with an increase in the cross-linking density).[15-19] However, this is offset by further increase in the degree of cross-linking that would, eventually, lead to lower degrees of interspersion between chains and junctions.[15-19] Hence, this will be accompanied by lower values of $[f^*]_c$ owing to lower values of the parameter κ, as predicted by Equation (8). Therefore, such transition is merely a transition between the affine and phantom limits of deformation as the network cross-linking density increases.

In Figure 2, the dashed line represents calculations based on the constrained junction model, calculated according to Equations (6) and (8).[23] Apparently better agreement with theory is obtained at relatively lower values of νRT. Deviation at higher values of νRT may be attributed to the different schemes utilized to obtain values of the parameters κ and ζ.[19] Queslel and Mark have discussed this matter in greater details.[19] Also, there has been some evidence that in the networks under investigation, higher values of the parameter ζ are required to obtain better fit with the theory, contrary to networks having lower functionalities where $\zeta \approx 0$.[21] Further investigation of this subject is now in progress. Our interpretations, thus presented, are in accord with the main premises of the Flory-Erman theory.[15-18]

Figure 3 is a plot of G against νRT for high functionality networks formed such that they have low extent of reactions of the vinyl groups $P_{vi} \approx 0.4$–0.9. The solid line represents the upper bound of theory for the bimodal affine network, according to Equation (9). A good fit is obtained at low values of νRT that corresponds to coincidence of experimental values of G with calculated theoretical values of the affine modulus. Again the data, so presented, do not unambiguously suggest any discernible intercept with the ordinate. At relatively higher values of νRT, the results manifest an unmistakable departure in the values of G from the upper (affine) bound of the theory toward the phantom limit.

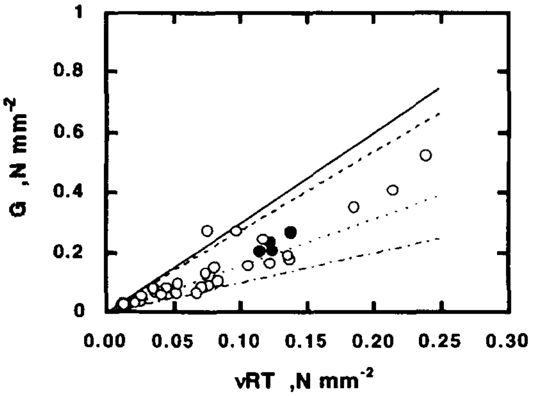

FIGURE 3 The shear modulus G for networks having low extents of reaction of the vinyl groups, as approximated by $2C_1 + 2C_2$, shown as a function of νRT (a measure of the degree of the cross-linking obtained from the end-linking chemistry). The circles represent results that were obtained by Kirk *et al.*,[5] and the filled triangles by Llorente and Mark.[1] See legend to Figure 2.

Such observation, in our opinion, can be reasonably attributed to the fact that at low extents of reaction not all the vinyl terminated chains will be attached to junctions at both ends. This, in turn, would lead to an increase in the number of elastically ineffective chains (more specifically, dangling ends) whose number is expected to increase with a decrease in P_{vi}. In such networks, lower values of P_{vi}, are expected to result in lower values of the effective functionality and so the chemical network density as measured by νRT. Values of the volume fraction of the elastically effective chains, v_2 and $2C_2$ are reported in Table I. Comparisons among the values of v, shows, clearly, that they are smaller for networks having low extents of reaction of the vinyl group P_{vi} than for those with higher extent of reaction. This phenomenon is clearly elucidated further in Figures 4–6. In Figure 4, values of $2C_2$ plotted against νRT. When thus plotted, the points for the networks having low extents of reaction are unmistakably lower. It is then clearly apparent

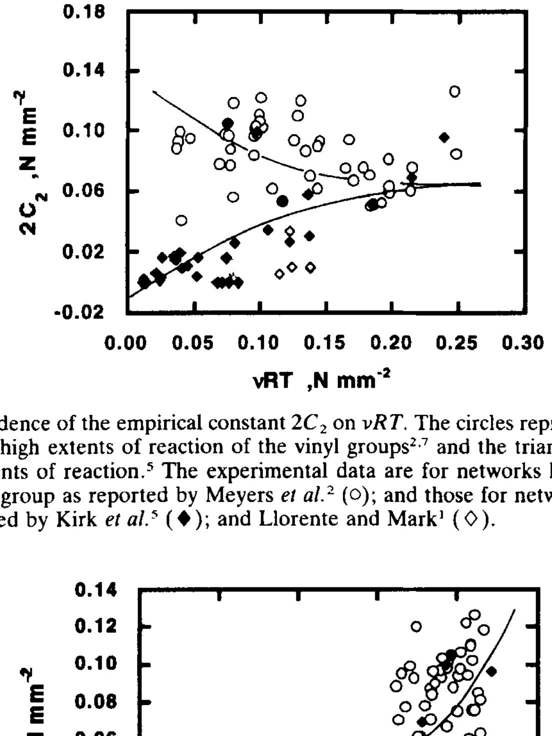

FIGURE 4 Dependence of the empirical constant $2C_2$ on νRT. The circles represent results obtained for networks having high extents of reaction of the vinyl groups[2,7] and the triangles are those for the ones with lower extents of reaction.[5] The experimental data are for networks having high extents of reaction of the vinyl group as reported by Meyers *et al.*[2] (○); and those for networks with low extents of reaction as reported by Kirk *et al.*[5] (◆); and Llorente and Mark[1] (◇).

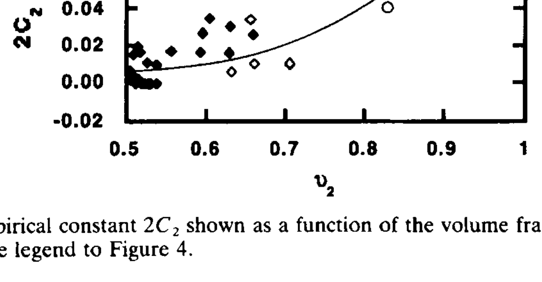

FIGURE 5 The empirical constant $2C_2$ shown as a function of the volume fraction of the elastically effective chains v_2. See legend to Figure 4.

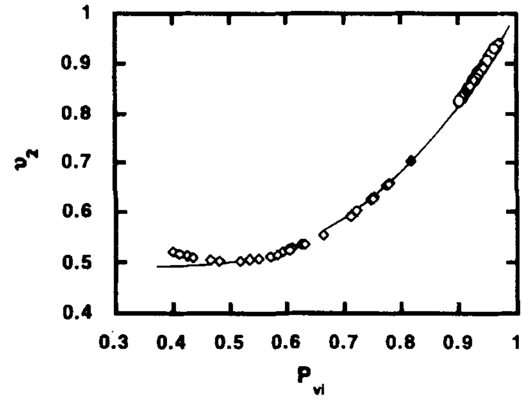

FIGURE 6 The volume fraction v_2 of the elastically effective chains in the dry unswollen state shown as a function of P_{vi}. See legend to Figure 4.

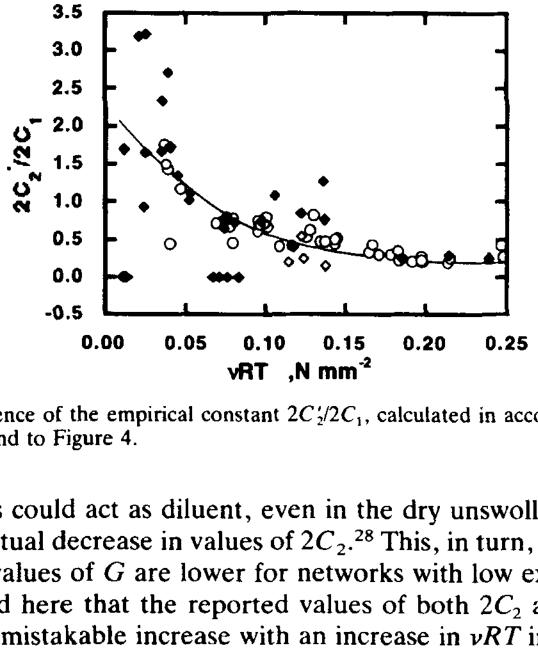

FIGURE 7 Dependence of the empirical constant $2C_2'/2C_1$, calculated in accordance with Equation (19) on νRT. See legend to Figure 4.

that dangling ends could act as diluent, even in the dry unswollen state, and thus leading to an eventual decrease in values of $2C_2$.[28] This, in turn, offer a reasonable explanation why values of G are lower for networks with low extents of reaction.

It is to be noted here that the reported values of both $2C_2$ and the ratio $2C_2/2C_1$ showed an unmistakable increase with an increase in νRT in networks having low extents of reaction.[5] This is clearly demonstrated in Figure 4. Such observation is at variance with all theoretical predictions.[1-7,14-19] Following the foregoing arguments, it can be explained, however, on the same grounds.

Our revised interpretation could also explain the observation that some of the experimental values of the constant $2C_2$ for networks with high extent of reaction were not as small as expected.[1-7] This phenomenon is clearly manifested in Figure 4. Specifically, values of $2C_2$ are in qualitative agreement with the theory; however, they are higher than the expected value of zero. In this connection, the bimodal networks being considered have two moles of short chains with $\phi = 3$ for each mole of long chains with ϕ probably greater than 10 or so. Because of their being

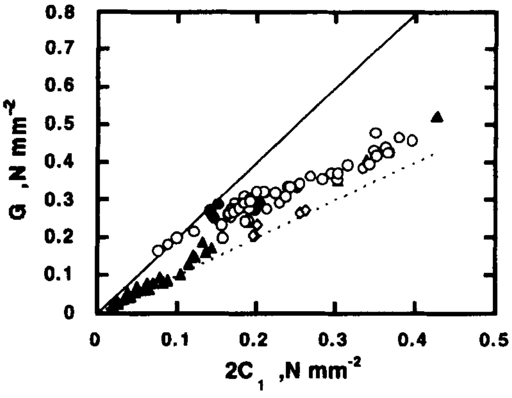

FIGURE 8 The shear modulus G, as approximated by $2C_1 + 2C_2$, shown as a function of $2C_1$ (the Mooney estimate of the high deformation modulus). The solid line is for the affine limit for an imperfect network as approximated by $2 \times (2C_1)$, calculated according to equation (23). The dotted line is for $2C_1$ itself. The filled circles represent results that were obtained by Opperman and Rehage.[7] See legend to Figure 4.

attached to junctions of functionality three and their decreased interpenetration, the suppression of the fluctuations associated with the short chains will be much less than those associated with long chains attached to junctions of very high functionality.[21,22]

Figures 5 and 6 lend further support to our statements. The results, so portrayed, confirm how lower extents of reaction P_{vi} would inadvertently result in lower values of v_2 as well as those of $2C_2$. In any case, the dependence of $2C_2$ on the volume fraction of the elastically ineffective chains that inadvertently act as a diluent is now established.

In this connection, Flory and Tatara[29] expressed the dependence of the reduced stress $[f^*]$ on the volume fraction of diluent by a modified form of the Mooney-Rivlin relationship which can be expressed as follows:

$$[f^*] = 2C_1 + 2C_2\alpha^{-1} = 2C_1' + 2C_2'v_2^{(4/3)-m}\alpha^{-1} \tag{18}$$

where

$$2C_2' = 2C_2/v_2^{(4/3)-m} \tag{19}$$

$$2C_1' = 2C_1 \tag{20}$$

Several investigators found $m = 0$.[29] On the other hand, more recent results indicated $m = 1/2$.[29] As discussed before, it has been observed that $2C_2$ decreases with swelling.[19,26] The results for various experiments for a range of degrees of swelling appeared to follow Equation (18) with $m = 1/2$ and were in qualitative agreement with the preceding equation.[29] The foregoing treatment obviates the conventional scheme of assigning separate values to $2C_2$ at each of dilution for a given sample.

Values of $2C'_2$ and the more relevant ratio $2C'_2/2C_1$ were obtained in accordance with Equation (19) with m assigned the value 1/2. In Figure 7, values of $2C'_2/2C_1$ are represented against νRT. When thus plotted, the various sets of points for all samples are found to conform to a single functional relationship (Equation 19) regardless of the volume fraction v_2 of the elastically effective chains of each sample in the dry unswollen state. As such, it is now clearly apparent that the network imperfections act as diluent. These results confirm and extend our predictions that such inherent imperfections would have a pronounced effect on the network elastomeric properties. In any case such behavior reflects a real network property and the fact that $2C_2$ decreases with dilution provide further evidence that the parameter $2C_2$ is essentially a topological contribution and contains no contributions from the chemical network.

Therefore, accurate values of the reported values of the moduli would be given justifiably by inclusion the volume fraction v_2 of the elastically effective chains in the unswollen state in Equation (1). It follows that

$$[f^*]_{\mathrm{aff}} = \nu RT(V/V_0)^{2/3} v_2^{-1/3} \tag{21}$$

$$[f^*]_{ph} = (1 - 2/\phi)\nu RT(V/V_0)^{2/3} v_2^{-1/3} \tag{22}$$

(All values of G and $2C_1$ so represented in this text has been corrected accordingly). Consequently, when the factor $v_2^{1/3}$ is incorporated in Equation (1), values of G as well as $2C_1$ so obtained would be lower than those reported. The results thus presented offers further proof that the volume fraction $v_2^{-1/3}$ of elastically ineffective chains should be incorporated in calculations, even in the dry unswollen state.

Beyond any doubt, the results clearly demonstrate that the empirical constant $2C_2$ involves essentially the network topological contributions and contains no contributions from the chemical network. Also, such results offer an unambiguous verification that the enhancement of $[f^*]$ at $\alpha \to 1$ vanishes upon swelling, suggesting it is due to difficulties in reaching elastic equilibrium when the network chains are very long.[19,26] Moreover, a proof of our statement about the nullity of the intercept in Figure 2 could be provided by inclusion of the data points portrayed here at very low values of νRT into that figure. Finally, the behavior observed is within the limits of the constrained-junction theory of Flory and Erman.[15–18]

It is now clearly apparent that accurate determination of the network parameters requires the utmost control of stoichiometry. A straight-forward method to test the validity of the predictions of the theory of Flory and Erman consists of plotting $G = 2C_1 + 2C_2$ against $2C_1 \approx [f^*]_{ph}$. As previously discussed, $2C_1$ may be identified with $[f^*]_{ph}$, within limits set by inaccuracies in the Mooney-Rivlin procedure.[19] According to theory,[15–18] $[f^*]_{ph}$ holds for any network regardless of the functionality of its junctions and the possible presence of network defects. This quantity is proportional to the effective interconnectivity of the network and, therefore, can be used to define an effective number of chains ν and junctions μ, regardless of how incomplete the network formation.[15] Such a plot, including data obtained from the literature is demonstrated in Figure 8 for the networks having high extents of reaction. In the figure, the dashed line represents the lower bound of the theory, the phantom network, corresponding to values of $2C_1$. The dotted line represents the lower bound of the theory, the phantom network, corresponding to values of $2C_1$ itself. The solid line approximates the upperbound, the affinely-deforming network, calculated according to Equation (16) for an imperfect network it follows that

$$[f^*]_{\mathrm{aff}} = \nu RT = 2\xi RT = 2(2C_1) \tag{23}$$

The results are well represented within the two limits of deformation, namely the affine and phantom limits. Better fit is obtained at small values of νRT, as compared to Figure 2. Moreover, the values of G for networks having low extents of reaction approaches those of $2C_1$ because of the presence of numerous elastically ineffective chains that would act as a diluent. Again, as the degree of cross-linking is increased, a clear transition toward the lower bound (the phantom limit) is observed. This procedure circumvents complications in accurately determining molecular masses, functionalities, and inherent imperfections. Such difficulties can lead to inaccuracies in the determination of the network parameters. Moreover, the results so represented are in excellent agreement with Flory's[27] universal treatment of imperfect networks. Undoubtedly, such behavior reflects a real characteristic of elastomeric network.

In sum, this study provides further verification about the role played by the short chains between cross links along the junction precursor. Also, the small strain modulus of networks having high-functionality cross-links and covering a range in the extent of reaction of the vinyl groups $P_{\nu i}$ can be successfully interpreted using the constrained junction theory. Taking into account the decrease in the degree of interpenetration as the degree of cross-linking increases offered a reasonable explanation for the departure of the values of the small-strain modulus from those for an affine network as well as the transition observed between the affine and the phantom limits of deformation. Also, the role played by the network imperfections has been clearly demonstrated. Apparently, the results at hand ascertain that the volume fraction of the elastically ineffective chains must be taken into consideration, even in the dry unswollen state, if quantitative significance is to be ascribed to the results of equilibrium elastic measurements. Additional critical comparisons should be concerned with the application of the constrained chain theory.[30] The present investigation, thus, represents another example of the wide applicability of the constrained junction theory for elastomeric polymer networks.

Acknowledgment

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