Swelling equilibrium characterization of high *cis*-1,4-polyisoprene networks and comparison with mechanical analysis

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Swelling equilibrium experiments with benzene and cyclohexane were performed on three series of high *cis*-1,4-polyisoprene (Shell IR307) networks. The influence of crosslinking density was studied by varying the amount of dicumyl peroxide used as crosslinking agent. Interpretation of the results through the constrained junction theory proposed by Flory and Erman was in agreement with a recently published characterization of these networks by stress–strain measurements in uniaxial extension. An interaction parameter χ for the *cis*-polyisoprene + cyclohexane system at 20°C was estimated to be 0.31 in the polymer volume fraction range 0 to 0.2.

(Keywords: polymer networks; swelling equilibrium, constraints on junctions; interaction parameter; equilibrium stress; uniaxial extension; benzene; cyclohexane)

INTRODUCTION

Swelling by an organic solvent is one of the simplest methods for characterizing elastomeric networks, rivalling stress–strain measurements in simplicity[1]. Such swelling involves two thermodynamic phenomena: an increase of the entropy of the network–solvent system due to the introduction of small molecules of diluent, and a decrease of the entropy of the polymer chains due to isotropic deformation. For the first effect, the mixing of polymer and solvent was successfully accounted for by the the liquid lattice theory of Flory and Huggins[2–4]. Use of their relationship and a statistical mechanical expression for the Gibbs elastic free energy change with dilation lead Flory and Rehner to propose a relation between swelling and degree of crosslinking[5–7] for an affine network (one in which the crosslinks move linearly with the dimensions of the elastomeric sample). Their equation has been widely used to characterize a variety of networks[8]. The molecular treatment of rubberlike elasticity has been improved by Flory and Erman[9,10], including detailed swelling–structure relationships[11–15]. In a preceding paper[16], it was shown that Flory and Erman's elasticity theory, treating entanglements as a restriction on junction fluctuations, could be reasonably used to determine the structure of *cis*-polyisoprene polymers cured with dicumyl peroxide by analysis of equilibrium stress–strain relationships in uniaxial extension. In the present paper are reported swelling equilibrium measurements performed on the same series of networks. Interpretation of these data through constrained junction theory applied to swelling equilibrium is compared with previous mechanical analysis.

ELASTICITY THEORIES AND SWELLING EQUILIBRIUM EQUATIONS

In the idealized phantom network model, chains may move freely through one another[17], junctions fluctuate around their mean positions due to Brownian motion, and these fluctuations are independent of deformation. In real networks, diffusion of junctions may be severely restricted by neighbouring chains sharing the same region of space. The extreme case is the affine network where fluctuations are completely suppressed and the instantaneous distribution of chain vectors is affine in the strain[18]. Significant experimental departures from phantom and affine model predictions have been recorded and the first theoretical attempts to account for these discrepancies were due to Ronca and Allegra[19] and Flory[18]. Particularly noteworthy is the molecular theory of Flory and Erman[9,10,20–22]. In their model, the restrictions of junction fluctuations due to neighbouring chains are represented by domains of constraints. In a later theoretical refinement, the behaviour of the network is taken to depend on two parameters, the most important being κ, which measures the severity of entanglement constraints relative to those imposed by the phantom network. Another parameter (ζ) takes into account the non-affine transformation of the domains of constraints with strain. On the plausible grounds that the constraints on junctions are determined by the degree of interpenetration of the chains about the junctions in the network, the parameter κ and the number of junctions μ in volume V_0 of the state of reference should be related[23] according to:

$$\kappa = I\langle r^2\rangle_0^{3/2}(\mu/V_0) \qquad (1)$$

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Table 1 Characterization of the *cis*-polyisoprene vulcanizates

Sample	$10^{-5}M_n$ (g mol^{-1})	Dicup,[a] x	$10^5\mu_t/V_0$ (mol cm^{-3})	μ_m/μ_t,[b] mechanical	ζ[b]	V_{2m},[c] benzene	κ[d]	$10^{-3}M_c$,[d] (g mol^{-1})	μ_s/μ_t,[d] swelling	V_{2m},[e] cyclohexane	χ_c[f]
1IR360	3.60	1.0	3.34	2.87	0	0.183	4.66	4.45	3.03	0.165	0.313
2IR360	3.60	0.8	2.67	3.23	0.011	0.171	4.97	5.07	3.31	0.154	0.315
3IR245	2.45	0.35	1.18	3.44	0	0.118	6.86	10.21	3.63	0.107	0.328
1IR125	1.25	1.2	4.00	2.62	0	0.183	4.40	4.13	2.66	0.159	0.295
2IR125	1.25	0.6	2.01	3.21	0.035	0.138	5.49	6.70	3.20	0.120	0.307
3IR125	1.25	0.45	1.51	3.08	0.010	0.117	6.24	9.02	3.10	0.105	0.324
4IR125	1.25	0.3	1.01	3.65	0.016	0.097	6.96	11.76	3.48	0.031	0.300

[a] Weight per cent in bulk
[b] Determined by analysis of stress–strain isotherms
[c] Volume fraction of polymer at swelling equilibrium in benzene at 20°C
[d] Determined by analysis of swelling equilibrium results in benzene
[e] Volume fraction of polymer at swelling equilibrium in cyclohexane at 20°C
[f] Calculated interaction parameter for the polyisoprene + cyclohexane system at 20°C

The quantity $\langle r^2\rangle_0$ is the mean-square end-to-end distance of the (non-perturbed) network chain. For *cis*-polyisoprene, the relationship between $\langle r^2\rangle_0$ and the average molecular weight M_c of the crosslinked network chains is[24]:

$$\langle r^2\rangle_0 = 3.8\times 10^7 M_c/N_A \qquad (2)$$

where N_A is Avogadro's number. The quantities M_c and $\langle r^2\rangle_0$ are expressed in g mol^{-1} and cm^2, respectively. In a previous paper[16], a universal value of 0.50 for the interpenetration parameter I was confirmed and an interpretation of parameter ζ in terms of network inhomogeneity was tentatively given.

The equation describing swelling equilibrium of a tetrafunctional network in the Flory–Erman model is[1,15]:

$$\ln(1-V_{2m})+V_{2m}+\chi V_{2m}^2 = -\left(\frac{\xi}{V_0}\right)V_1 V_{2m}^{1/3}[1+K(V_{2m}^{-2/3})] \qquad (3)$$

where V_{2m} is the polymer volume fraction at swelling equilibrium, χ the polymer–solvent interaction parameter and V_1 the molar volume of solvent. The function K depending on κ and ζ is defined in ref. 10 (equation (37)). The quantity ξ is the cycle rank or number of independent circuits in the network, and subsumes all aspects of network imperfections[18,22,25].

For randomly crosslinked networks, Queslel and Mark[1,26] have proposed the following relationships between the cycle rank ξ, the total number of junctions μ, the average molecular weight M_c of network chains and the number-average molecular weight M_n of the polymer precursor:

$$\frac{\xi}{V_0} = \left(\frac{\rho}{2M_c}\right)\left(1-3\frac{M_c}{M_n}\right) \qquad (4)$$

$$\frac{\mu}{V_0} = \left(\frac{\rho}{2M_c}\right)\left(1-\frac{M_c}{M_n}\right) \qquad (5)$$

where ρ is the polymer density.

According to the theory outlined above, the affine network model corresponds to the limit $\kappa\rightarrow\infty$ and $\zeta\rightarrow 0$ whereas the phantom state is reached when $\kappa\rightarrow 0$ and $\kappa\zeta\rightarrow 0$.

The swelling equation for an affine network is then deduced from equation (3) as:

$$\ln(1-V_{2m})+V_{2m}+\chi V_{2m}^2 = -\left(\frac{\xi}{V_0}\right)V_1 V_{2m}^{1/3}\left[1+\left(\frac{\mu}{\xi}\right)(1-V_{2m}^{2/3})\right] \qquad (6)$$

For a phantom network:

$$\ln(1-V_{2m})+V_{2m}+\chi V_{2m}^2 = -\left(\frac{\xi}{V_0}\right)V_1 V_{2m}^{1/3} \qquad (7)$$

MATERIALS AND METHOD

Samples were generously provided by Manufacture Française des Pneumatiques Michelin. The precursor polymer was an anionic commercial polyisoprene (Shell IR307) with a high *cis*-1,4 configuration (92% *cis*, 5% *trans*) and T_g (d.s.c.) = −60°C. Three batches of varying number-average molecular weight, namely $M_n = 3.60\times 10^5$, 2.45×10^5 and 1.25×10^5 g mol^{-1}, were prepared by degradative work on a two-roll mill. Each precursor was mixed in bulk with several amounts of pure dicumyl peroxide, moulded and cured. Curing conditions (30 min at 170°C) were chosen to ensure full decomposition of the peroxide with negligible chain scission during curing. Designation of vulcanizates, number-average molecular weight of precursor polymer and quantity of peroxide are reported in *Table 1*.

Samples to be used in swelling equilibrium experiments were extracted first to remove any soluble materials and then dried and weighed. They were then placed into benzene (or cyclohexane) at 20°C and periodically reweighed swollen until constant weight was observed, equilibrium being achieved at this point. The extent of swelling was characterized by V_{2m} (calculated by assuming additivity of volumes), the volume fraction of polymer in the network at maximum (equilibrium) swelling. Values of V_{2m} are reported in *Table 1* for the seven investigated networks swollen with either benzene or cyclohexane.

An error range of $\pm 10^{-3}$ was estimated for V_{2m} after reproducibility experiments.

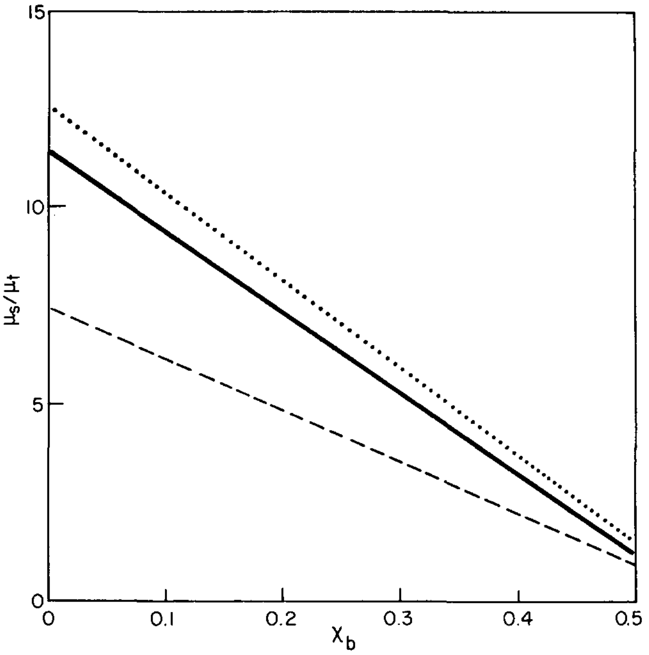

Figure 1 Influence of the elasticity model and of the interaction parameter χ_b on the ratio μ_s/μ_t for the 2IR360 vulcanizate swollen with benzene: (———) real network model; (– – –) affine network; (·····) phantom network

RESULTS AND DISCUSSION

The characterization of network structure by analysis of mechanical properties with an elasticity model gives some insight into the chemical crosslinking process. Indeed the number density of junctions μ_m/V_0 determined by this analysis may be compared with the number density of junctions μ_t/V_0 calculated with the knowledge of the initial amount x (weight per cent) of peroxide assuming full decomposition of peroxide and a 1:1 crosslinking efficiency. The quantity μ_t/V_0 is related to x through:

$$\mu_t/V_0 = \rho x/[270(100+x)] \qquad (8)$$

The quantity μ_t/V_0 and the ratio μ_m/μ_t determined in a previous paper[16] by mechanical analysis are reported in *Table 1* for the seven vulcanizates.

Influence of elasticity model and interaction parameter on network structure determination

Network characterization through swelling measurements is very sensitive to the elasticity model and interaction parameter used in the calculations. As an example, the swelling measurement of 2IR360 vulcanizate in benzene has been interpreted through Flory–Erman, affine and phantom network models. The ratio μ_s/μ_t and the molecular weight M_c were calculated as a function of interaction parameter χ_b through equations (1) to (5) for a Flory–Erman network, equations (4) to (6) for an affine network, and equations (4) and (7) for a phantom network. The values of μ_s/μ_t and M_c are reported in *Figures 1* and *2*, respectively. These figures show the great sensitivity of network characterization to the choice of elasticity model and interaction parameter. Use of an inadequate elasticity model may serve at most to the ranking of series of network of the same polymer, according to their crosslinking densities. In *Figure 2*, the molecular weight M_c calculated with a phantom model is lower than M_c for an affine one. In a phantom model, junction fluctuations decrease the impact of chain entropy changes. It is therefore necessary to have a phantom network with a higher density of crosslinks or a smaller M_c to counteract this effect and to give the same elastic contribution as in an affine network.

The Flory–Erman constrained junction treatment has already been applied successfully by Erman and Baysal[27] to interpret swelling equilibrium data. However, one must bear in mind that, as shown by Gottlieb and Gaylord[14], no model available in the literature was able to reproduce quantitatively the maximum in the dependence of $\lambda \ln(a_1^c/a_1^u)$ on λ (where λ is the isotropic deformation $V_2^{-1/3}$, V_2 being the volume fraction of polymer in the polymer–solvent system, and a_1^u and a_1^c the solvent activities respectively in uncrosslinked and crosslinked polymers)[1].

In the present paper, the interaction parameter χ_b for the natural rubber + benzene system at 25°C determined by Eichinger and Flory[28] is used. It may be approximated by the following linear function of V_{2m}:

$$\chi_b = 0.39 + 0.04 V_{2m} \qquad (9)$$

This equation differs slightly from that proposed previously by Queslel and Mark[24] because they used segment fractions instead of volume fractions of polymer.

Characterization of cis*-polyisoprene networks by swelling equilibrium in benzene and comparison with mechanical analysis*

The values of V_{2m} for the networks swollen in benzene

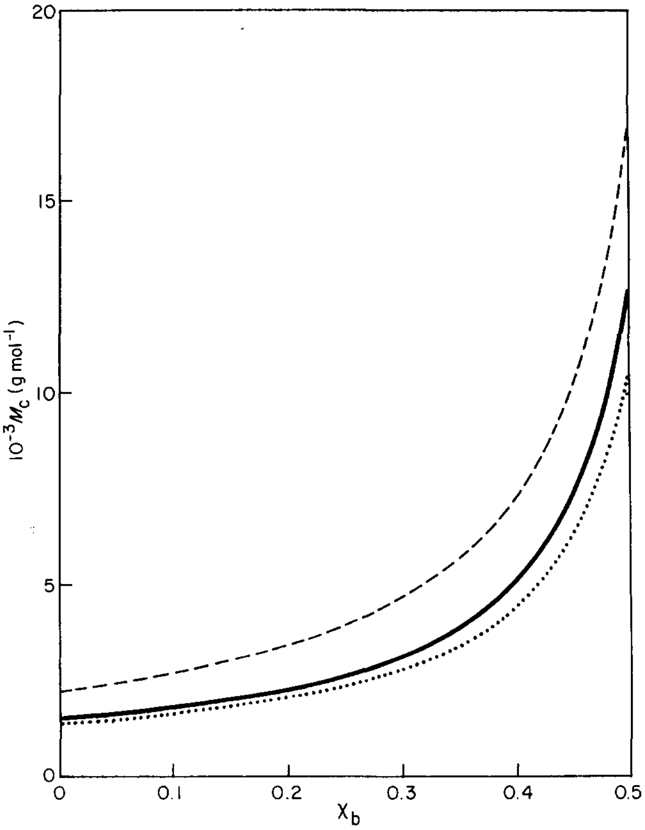

Figure 2 Influence of the elasticity model and of the interaction parameter χ_b on the molecular weight M_c for the 2IR360 vulcanizate swollen with benzene: (———) Flory–Erman real network model; (– – –) affine network; (·····) phantom network

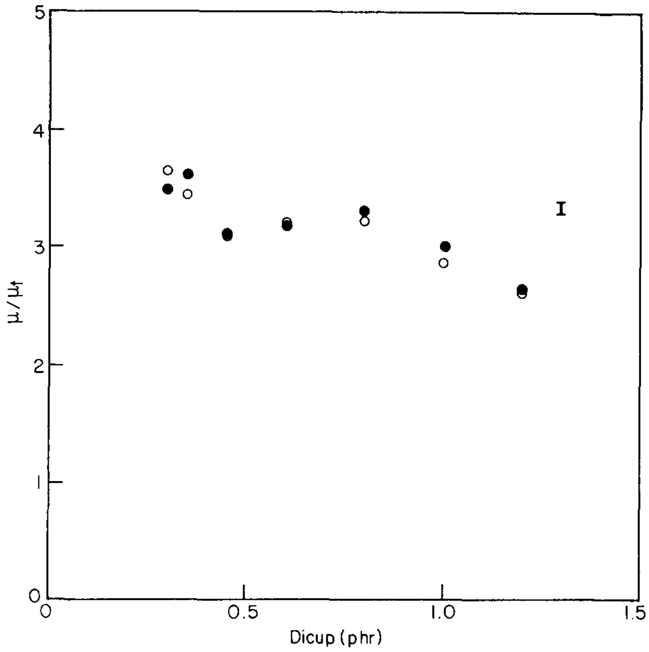

Figure 3 Comparison between the ratios μ/μ_t determined by mechanical (○) and swelling (●) analysis as a function of initial amount of dicup (parts per hundred parts rubber). The error bar was estimated from the error involved in polymer volume fraction determination after network swelling with benzene

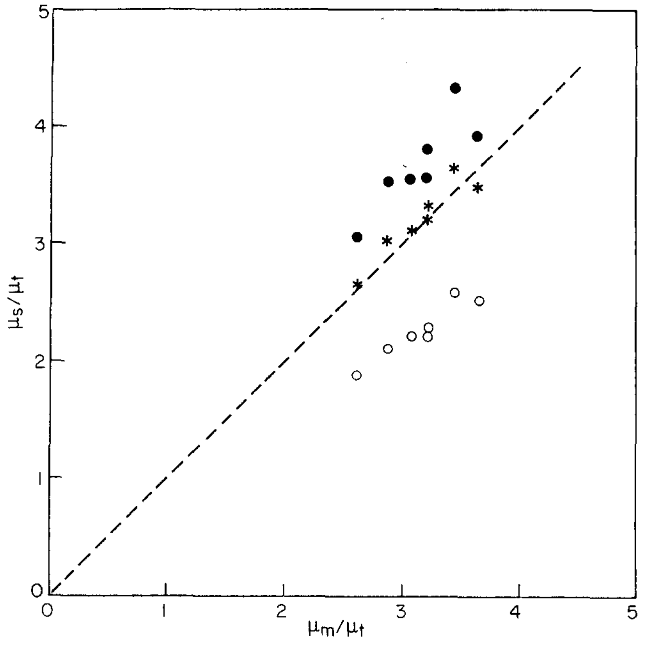

Figure 4 Influence of the elasticity model used to analyse swelling equilibrium data on μ_s: (●) phantom; (∗) Flory–Erman; (○) affine. The value of μ_m was calculated from mechanical data through the Flory–Erman model. The broken line represents perfect agreement between swelling and mechanical characterizations

were used to determine the molecular weight M_c by combining equations (1) to (5) and (9) and solving the resulting equation with respect to M_c. Parameter ζ was chosen equal to that determined previously by mechanical analysis. It has little effect on the final results. The values of κ and μ_s/μ_t were then calculated by making use of equations (1), (2), (5) and (8). Their values are reported in *Table 1*.

Of particular interest is the comparison between the crosslink densities μ determined either by swelling equilibrium (in this paper) or mechanical analysis[16]. These quantities normalized with respect to μ_t are reported in *Figure 3* as a function of initial amount of dicumyl peroxide (dicup). The error bar was estimated from the uncertainty in the determination of V_{2m}. As shown in *Figure 3*, the two sets of data are quite consistent. To evaluate the influence of the elasticity model, we have interpreted the swelling equilibrium data with the phantom, Flory–Erman and affine models. The ratios μ_s/μ_t thus obtained are plotted *versus* μ_m/μ_t in *Figure 4*. We kept the values of μ_m calculated through the Flory–Erman model since phantom and affine models cannot reproduce the observed decrease of reduced stress with increasing strain in the Mooney–Rivlin plot[16]. The broken line in *Figure 4* represents perfect agreement between swelling and mechanical characterizations. This agreement is quite satisfactory if the Flory–Erman model is also used to interpret swelling measurements. It is thus clearly demonstrated that swelling equilibrium and equilibrium stress–strain analysis lead to equivalent network structure characterizations if an adequate elasticity model (such as the Flory–Erman theory) and interaction parameter are used for these analyses.

Determination of interaction parameter for the cis-*polyisoprene + cyclohexane system at 20°C*

From the network structures determined above and from the swelling measurements in cyclohexane reported in *Table 1*, it was possible to calculate the interaction parameter χ_c for the *cis*-polyisoprene + cyclohexane system. A similar procedure was applied by Erman and Baysal for the polystyrene + toluene and polystyrene + toluene + methanol systems[27].

The value of χ_c was calculated by solving equation (3) while ascribing to κ, ζ, μ and M_c the values previously determined by swelling with benzene and reported in *Table 1*. The cycle rank ξ was calculated through equation (4). Values of χ_c for the seven vulcanizates were reported in *Table 1* and plotted with respect to volume fraction V_{2m} in cyclohexane in *Figure 5*. The data points are scattered

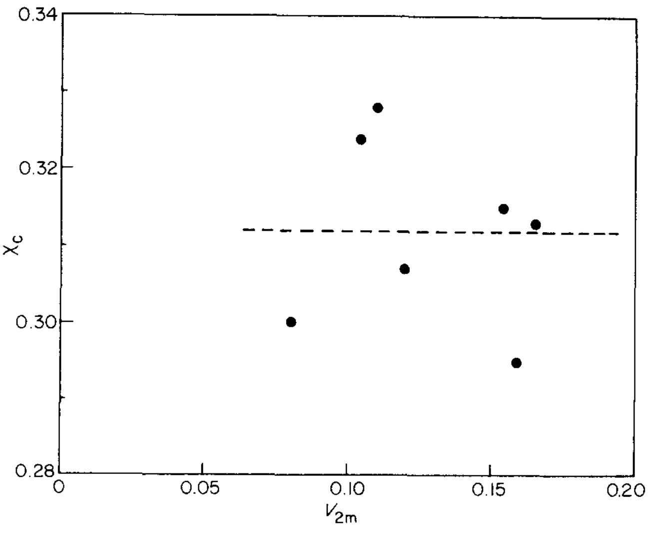

Figure 5 Calculated interaction parameter χ_c for the *cis*-polyisoprene + cyclohexane system at 20°C as a function of polymer volume fraction V_{2m}. The broken line represents an average value of 0.312

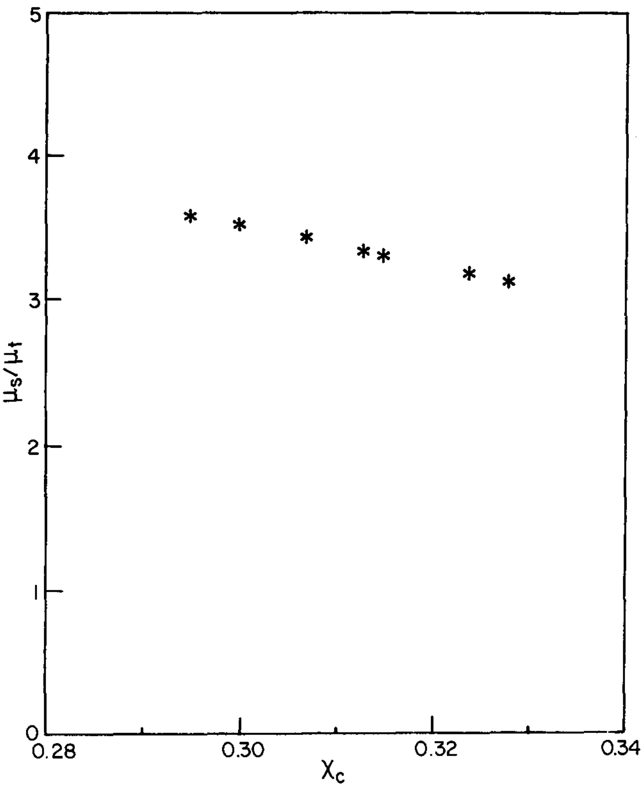

Figure 6 Estimation of the maximum error on the ratio μ_s/μ_t for the 2IR360 vulcanizate swollen with cyclohexane caused by the scattering in the calculated values of χ_c represented in *Figure 4*

around an average value of 0.31. It was noteworthy that an approximately similar amount of scattering was obtained if network characteristics determined by mechanical analysis[16] were used instead of those determined by swelling in benzene.

Another way to illustrate the scattering in *Figure 5* is to calculate the ratio μ_s/μ_t of, for example, the 2IR360 vulcanizate by using successively for the interaction parameter χ_c the values previously determined for the seven networks. The value of μ_s/μ_t is plotted as a function of χ_c in *Figure 6*. The resulting scattering is quite reasonable in view of the different cumulative errors involved in the overall procedure, i.e. uncertainties on the determination of V_{2m} in benzene and then in cyclohexane. It can be concluded that it is a good approximation to use 0.31 for the interaction parameter χ_c for the *cis*-polyisoprene + cyclohexane system at 20°C in the polymer volume fraction range 0 to 0.2.

CONCLUSIONS

The structure of *cis*-polyisoprene networks was characterized by analysis of swelling equilibrium measurements in benzene with Flory and Erman's constrained junction model of elasticity and with an interaction parameter independently determined by Eichinger and Flory by high-pressure osmometry and differential solvent vapour sorption techniques. The results were in agreement with those deduced previously by interpretation of equilibrium stress–strain relationships with the same elasticity model. An average interaction parameter of 0.31 was calculated for the *cis*-polyisoprene + cyclohexane system.

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