structural formations may contain two specific molecular motions: translational motion along the chain direction and rotational motion with respect to chain axis. The chain molecules are able to reject noncrystallizable counits if the transitions are slow enough and the chemical compositions are favorable. (3) Two transition processes have been observed: a fast process, which can be characterized by solidification, and a slow process, which is close to a normal crystallization process. The experimental data of the latter case can be cast in an Avrami equation. However, the apparent coefficient n here is very low. It may be caused by the decrease of radial crystal growth rate due to the hindering of previously formed crystals and a reduction in molecular mobility. (4) Thermodynamic properties of the copolymers at their metastable equilibria have been estimated. Both low heats of the transition and entropies of the transition reveal that chain packing in the crystals is far from perfect, and chain conformations do not change very much during the transitions from nematic melts to condis crystals.

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Registry No. (HBA)(HNA) (copolymer), 81843-52-9.

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Modulus of Polybutadiene Networks Made by Hydrosilation Cross-Linking

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ABSTRACT: In this work we studied the effect of the topological interactions between polymer chains by measuring the small deformation modulus of polybutadiene networks. The networks were prepared by linking pendant double bonds (vinyls) on the polybutadiene with *p*-bis(dimethylsilyl)benzene catalized by platinum(II). Model reaction studies with a hexene and hexadiene mixture and a low molecular weight polybutadiene showed that this cross-linking reaction is complete and free of side reactions when the pendant double bonds are in excess. With silane in excess the backbone double bonds also react. Two monodisperse polybutadienes with different vinyl content and plateau moduli were linked with the same reaction. The small strain modulus measurements for the networks were better explained by including the effect of topological interactions along the contour of the network chains. The effect of interactions on the junction points was smaller that found by Dossin and Graessley for polybutadienes cross-linked by radiation.[1]

Introduction

While the basic concepts of the theory of rubber elasticity have long been well established, the effect of topological interactions between network chains (entanglements) is still a subject of controversy.[2–4]

It is generally accepted that topological interactions have a localized effect on the mobility of the junction points by suppressing the fluctuations of the cross-linking junction about its average position.[5] Following Graessley's work we can express the small deformation modulus as[1]

$$G = (\nu - h\mu)RT \qquad (1)$$

where G is the modulus of the network at small deformations, ν is the concentration of elastically active strands,

μ is the concentration of elastically active junction points, R is the gas constant, T is the absolute temperature, and h is related to the mobility of the junction points and is an empirical constant between 0 and 1. This equation contains the limits of the classical theory of elasticity, the "phantom network" when $h = 1$ (no suppression of the fluctuations), and the "affine model" when $h = 0$ (complete suppression of the fluctuations). Graessley's h can be connected to the parameter κ of the Flory model.[2,6,7]

The classical theory does not take into account the contribution that long-range topological interactions between the chains can make to the modulus. If during the cross-linking reaction, part of the entanglements are permanently trapped, they will not be able to relax and an additional contribution to the modulus of the network should be added. In that case eq 1 becomes

$$G = (\nu - h\mu)RT + T_e G_e \tag{2}$$

where T_e is the fraction of topological interactions permanently trapped by the cross-linking process and G_e is the small strain modulus of the entanglement network, closely related to G_N^0 the plateau modulus of the linear polymer.[8]

The aim of this work is to test this last contribution, which has been the subject of a long controversy since its statement by Langley,[8] and to check the local effect of the topological interactions on the mobility of the junctions.

For this purpose, a chemically cross-linked system was chosen to avoid the problems that usually arise when radiation cross-linking is used, such as possible chain scission and formation of multifunctional junctions. Nearly monodisperse, linear polybutadiene samples were cross-linked through the 1,2-butadiene units (vinyls), using a hydrosilation reaction:

$$\gt SiH + {-}CH{=}CH_2 \rightarrow \gt SiCH_2CH_2{-} \tag{3}$$

The selection of polybutadienes that have a high plateau modulus, several times that of the poly(dimethylsiloxane) (frequently used to test elastic theories) was expected to facilitate the determination of the effect of the topological interactions along the contours of the chains by testing the importance of the last term in eq 2.

The characterization of the starting materials and the study of the crosslinking reaction were performed to test the suitability of the system to be used as a model network. There exist two possible types of side reactions in this system: a) reactions including the silane groups, and b) rearrangement of the vinyl double bonds in the polybutadiene chains; both are discussed below.

Experimental Section

Polybutadiene Characterization. Three polybutadiene samples of very narrow molecular weight were used as starting materials. The two higher molecular weight samples (CM-1 and CM-3) were synthesized by L. J. Fetters of Exxon (Annandale, NJ), and the low molecular weight polymer (CM-5) was prepared by P. Lutz of Centre de Recherches sur les Macromolecules, CNRS (Strasbourg, France). All samples were obtained by anionic polymerization of butadiene with *sec*-butyllithium as initiator, leading to random addition of the butadiene units.

The microstructure of the polymer chains was determined by NMR. The content of 1,2 units was obtained from ^1H NMR, where the peak at 4.9 ppm is due to the contribution of the hydrogens in the vinyl groups ($=CH_2$) and the peak at 5.4 ppm corresponds to the hydrogens of the cis and trans units ($CH=CH$). Table I shows the different vinyl content of the samples. Molecular weights and polydispersities were measured by GPC using polybutadiene calibration.

Table I
Characterization of the Polybutadienes

	M_n[a]	M_w/M_n[a]	% vin[b]	G_N^0, MPa[c]	G_N^0, MPa[d]
CM-1	41 000	1.05	33	0.92(1)	0.70 ± 0.02
CM-3	27 000	1.03	8	1.17(2)	0.96 ± 0.03
CM-5	2 000	1.06	12		

[a] Measured by GPC, using polybutadiene calibration. [b] Mol % of 1,2-addition units in the polymer, measured by ^1H NMR. [c] From Carella et al.:[11] (1) 35% vinyls, T = 50 °C (Table IV);[11] (2) 8% vinyls, T = 100 °C (Table VII).[11] [d] Shifted to 60 °C.

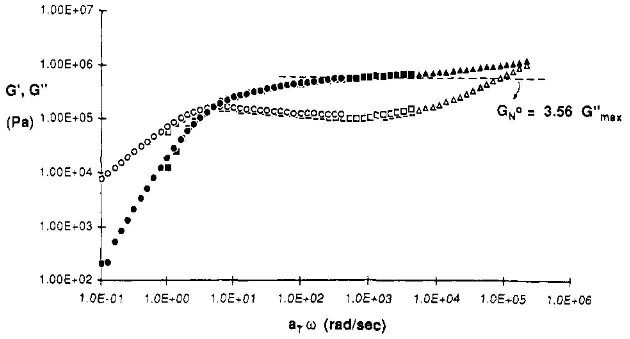


Figure 1. Composite curve for the polybutadiene CM-1 obtained from reducing modulus versus frequency data at a reference temperature of −20 °C. Open symbols, G'', filled symbols, G'; circles, −20 °C; squares, −40 °C; triangles, −60 °C.

The plateau modulus of the linear polymers was determined from measurements of G' and G''. A frequency sweep in the range 0.1–500 rad/s was carried out at different temperatures on the Rheometrics System IV under nitrogen atmosphere. The data were reduced to a master curve by using standard methods.[9] The use of the modulus scale shift ($\rho_{pbd}T/(\rho_{pbd}T)_0$) gave a better superposition than no shift at all. The curve obtained for CM-1 is shown in Figure 1. Raju et al. have evaluated the plateau modulus of linear entangled polymers with very narrow chain length distribution using the following equation applied to the terminal region only:[9,10]

$$G_N^0 = 2/\pi \int_{-\infty}^{\infty} G'' \, d \ln \omega \tag{4}$$

From the comparison of their results they proposed the use of the simpler expression

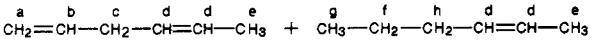
$$G_N^0 = 3.56 G''_{max} \tag{5}$$

The values obtained by using eq 5 are shown in Table I. This method was also used by Carella et al. who worked with polybutadienes of different vinyl content (8% up to approximately 99%) to study the relation between the microstructure of the chains and the viscoelastic properties of the material.[11] They found that the lower the vinyl content the higher the plateau modulus. Our measurements seem to follow this trend, although the absolute values were smaller than the values reported by Carella for similar polymers and conditions. To check our measurements one polybutadiene sample of high molecular weight (approximately 600 000) was tested by Dr. Fetters and sent to us. His and our results were G_N^0 = 1.2 MPa at 26 °C and 1.3 MPa at 20 °C, respectively, both calculated by using eq 5. The reasons for the differences between Carella's results and ours are not clear. They worked with polybutadienes of molecular weights about five times larger than our highest molecular weight sample. This could have affected the resolution of the G'' peak. We also needed to work at much lower temperatures (−20 to −80 °C) than Carella et al. (20 to 120 °C) to obtain data in that region. To shift our data at higher temperatures the factor $\rho_{pbd}T/(\rho_{pbd}T)_0$ was used again (i.e., G_N^0 = 0.57 MPa at −20 °C was shifted to 0.7 MPa at 60 °C for CM-1). Carella et al. found a smaller shift in the modulus scale than the one that we used and thus they decided not to include it.

CM-5 was a low molecular weight sample and used only as model compound in the study of the cross-linking reaction.

Model Reaction. Originally, hydrosilation reactions were considered to be ideal cross-linking reactions,[4,12] but subsequent studies showed that there are secondary reactions which consume

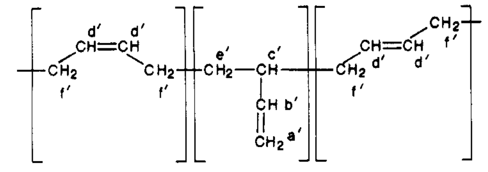
Table II
Assignment of ^{1}H NMR Peaks



$\overset{a}{CH_2}=\overset{b}{CH}-\overset{c}{CH_2}-\overset{d}{CH}=\overset{d}{CH}-\overset{e}{CH_3} + \overset{g}{CH_3}-\overset{f}{CH_2}-\overset{h}{CH_2}-\overset{d}{CH}=\overset{d}{CH}-\overset{e}{CH_3}$

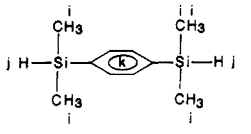
CM-H

a 4.9 ppm	e 1.65 ppm
b 5.65–5.8 ppm	f 1.45 ppm
c 2.75 ppm	g 0.9 ppm
d 5.4 ppm	h 2.0 ppm



CM-5

a′ 4.9 ppm	d′ 5.4 ppm
b′ 5.65 ppm	e′ 1.3 ppm
c′ 2.10 ppm	f′ 2.1 ppm (cis 1,4), 2.04 ppm (trans 1,4)



silane

i 0.34 ppm
j 4.4 ppm
k 7.54 ppm

the silane groups without forming linking points.[13] Most of these studies used siloxysilanes as cross-linkers and they found that the loss of silane is primarily due to siloxane–SiH bond redistribution, which leads to the formation of a new cross-linker of higher molecular weight and silanes of low molecular weight which are very volatile and are lost during the reaction.[14,15] This reaction seems to always occur when working with siloxysilane molecules and can account for as much as 20–30% of the silane groups. It was also noted that the presence of solvents and high temperatures tend to favor this side reaction.

Other side reactions can reduce the functionality of the polybutadiene by shifting the pendant double bonds to internal positions.[14,16]. Also, the functionality of the polymer can be increased if the 1,4-addition units react. It is generally accepted, however, that double bonds of the backbone of the chain are much less reactive than the vinyl groups.[17,18]

To test for secondary reactions, a mixture of hexene–hexadiene, which we will call CM-H, and a low molecular weight polybutadiene (CM-5) were chosen as model compounds. To prepare CM-H, 2-hexene, 99% pure, and 1,4-hexadiene (cis-trans), 99% pure, both purchased from Aldrich, were used. The hexene and hexadiene were mixed in a weight ratio of 0.67:1. Thus the mol fraction of terminal double bonds to total double bond groups was 0.377 and thus similar to the fraction of vinyls in the polybutadiene CM-1. The characteristics of CM-5 are summarized in Table I. The cross-linker used in this work is *p*-bis(dimethylsilyl)benzene, purchased from Petrarch, 98% pure as measured by GC in this laboratory. The catalyst is described in the Cross-Linking Reaction section, below. All reactants were used without further purification.

Each reactant was characterized by ^{1}H NMR. The solutions were prepared in deuteriated chloroform with 1% (v/v) of tetramethylsilane (TMS) as reference standard. Table II gives the corresponding peak assignment. Different amounts of silane were mixed with CM-H, so that the ratio terminal double bond/silane groups was r = 10, 5, 1, 0.5. The reactive samples were prepared in Teflon-lined screw-cap test tubes. The closed tubes were placed in an oil bath at 60 °C for 1 day. The weights of the samples were registered before and after the reaction to check for possible volatilization of the reactants but no appreciable loss of weight was observed. The solutions for ^{1}H NMR were prepared as mentioned above for the characterization of the reactants.

The samples were studied by ^{1}H and ^{13}C NMR. From the latter only qualitative results could be derived and are described below.

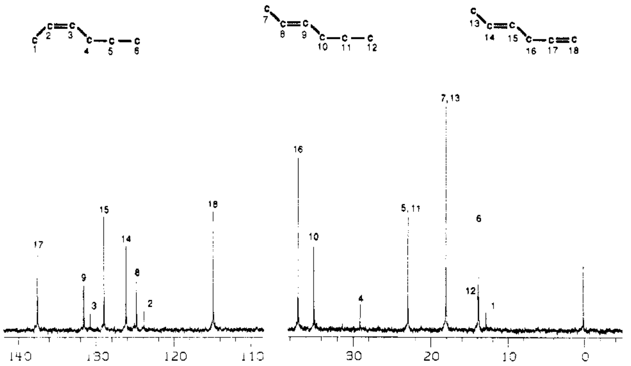


Figure 2. ^{13}C NMR spectra of CM-H with its corresponding peak assignments.

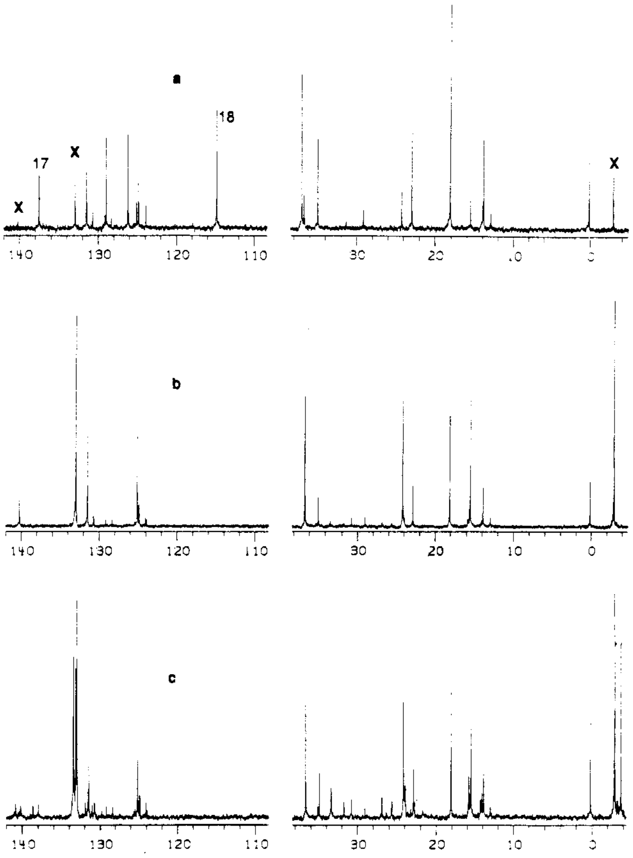


Figure 3. ^{13}C NMR spectra of reacted CM-H samples with increasing amounts of cross-linker (r [=] vin/sil): (a) r = 10; (b) r = 1; (c) r = 0.5. Peaks marked X correspond to the cross-linker.

Figure 2 shows the ^{13}C NMR spectra for CM-H and the corresponding peak assignment. For increasing amount of cross-linker (Figure 3), it can be seen that the peaks corresponding to the vinyl group disappear completely at r = 1. The peaks at 126 and 129 ppm due to the internal double bonds (CH=CH) in the hexadiene shift to 124.8 and 131.5 ppm when the terminal double bonds (vinyls) react. The cross-linker gives peaks at −3.9, 133.3, and 138.5 ppm. After reaction these peaks appear at −2.9, 132.9, and 140.1 ppm as it is seen in the figures. At r = 1 very weak peaks appear at 30.7, 27, and 25 ppm, suggesting that a secondary reaction might begin to take place at the stoichiometric balance. At r = 0.5 the presence of a secondary reaction is evident by the appearance of new peaks in the alliphatic region which can be explained by the reaction of internal double bonds, probably due to the reaction of the hexenes. The position of the peaks is coincident with that of the peaks that appear if pure 2-hexene is reacted with the cross-linker. Under identical conditions of reaction as for the CM-H hydrosilation, about 30% of the silanes react with the internal double bond of the hexene. It can be concluded from ^{13}C NMR results that when vinyls are in excess, there is no important contribution from side reactions.

Table III
Experimental versus Calculated Relative Area Peaks on Reacted Samples[a]

group	δ (ppm)	CM-H			CM-5	
		$r = 10$	$r = 5$	$r = 1$	$r = 0.5$	$r = 5.81$
$=CH_2$	4.9	9.0, 8.834 (−1.8)	4.0, 3.819 (−4.5)	0, 0	0, 0	4.81, 4.49 (−6.7)
$=CH-$, 1,4 units	5.4	16.58, 15.1 (−8.9)	8.25, 7.81 (−5.3)	1.654, 1.49 (−9.9)	0.833, 0.684 (−18.0)	42.57, 47.45 (11.5)
$=CH-$, 1,2 units	5.65	4.5, 4.11 (−8.7)	2.0, 1.77 (−11.5)	0, 0	0, 0	2.405, 2.347 (−2.4)
$>SiH$	4.4	0, 0	0, 0	0, 0	0.25, 0.17 (−32.0)	0, 0
$>SiCH_3$	0.34 or 0.24	3.0, 2.94 (−2)	3.0, 3.16 (5.3)	3.0, 2.89 (−3.7)	3.0, 2.82 (−6.0)	3.0, 3.14 (4.7)
$-CH_2-$, CM-H only	2	7.478, 6.958 (−6.9)	4.224, 4.228 (0.1)	1.654, 1.643 (−0.66)	0.995, 0.809 (−18.7)	

[a] The entries *a*, *b* (*c*) in the table represent, *a*; the relative area calculated assuming that hydrosilation takes place only through the vinyl groups; *b*; experimental value of the relative areas; and *c*; percentage difference, with respect to *a*.

The same samples were used for ^{1}H NMR studies. No effort was made to optimize delay time or flip angle during the data acquisition, but standard parameters were used instead. Thus the expected error in our data is on the order of 10%. However, the areas under the peaks can be used as a semiquantitative measurement of the relative concentration of the groups. All the areas were related to the peak at 7.5 ppm, which corresponds to the aromatic hydrogens of the cross-linker. Table III shows the comparison between calculated and measured relative area peaks. In general there is good agreement with the theoretical values calculated without considering any side reaction, except for the case of $r = 0.5$. At $r = 0.5$ the difference between calculated and measured areas is greater, in agreement with the ^{13}C NMR results. This suggests that the reaction of internal double bonds is important. At $r = 0.5$ (excess of silane), a split of the peaks at 7.5 and 0.34 ppm appears. a similar feature was observed in ^{13}C NMR. These splits are due to the fact that at complete conversion of the vinyls, there coexist in the sample silane molecules with both groups reacted, with neither group reacted, and with one group reacted and the other unreacted. In ^{1}H NMR the peak at 0.34 ppm corresponding to the methylene groups of the cross-linker is shifted at 0.24 ppm when the silane is reacted; in the same way the peak originally at 7.54 ppm (aromatic hydrogens in the cross-linker) is shifted to 7.48 ppm after the reaction. For all the samples the peak at 0.24 ppm (except at $r = 0.5$) appears as a single sharp peak which suggests that all the silane molecules have been consumed in the same type of bonding. As a test, the relative area of this peak is reported (Table III). ^{1}H NMR was also used on a network obtained from CM-5, at $r = 5.81$, where r is defined as the ratio of vinyl to silane groups. Again, the experimental data compare quite well with the theory.

In summary, the model reaction studies showed that no double bond or silane rearrangement reactions were present. The later seems reasonable since the aromatic silane is not expected to participate in the same kind of reactions reported for siloxysilane cross-linkers.[14] The only side reaction detected was the reaction of the 1,4-addition units with the silane and this occurred appreciably only when working in excess of cross-linker.

Cross-Linking Reaction. Due to the limited amounts of the polybutadienes, only small samples were prepared (about 2 g). Different proportions of polybutadiene and cross-linker were carefully weighed, the catalyst was added, and then the samples were mixed by hand with a spatula in a 30-mL jar for 3–5 min. The catalyst used was *cis*-dichlorobis(diethyl sulfide)platinum(II) (Strem Chemicals, Inc.) prepared as a solution 0.5% by weight in toluene. At most 100 ppm of platinum were used to catalyze the reaction. In the case of large stoichiometric imbalances a certain amount of polybutadiene and cross-linker was premixed, then the remaining polybutadiene and the catalyst were added and the sample was mixed again. These samples were about 4–5 g.

For some samples a DSC run was used to check the mixing. Samples of about 25 mg were used for scanning at 10 °C/min under nitrogen atmosphere. The samples showed a single exothermic peak at about 90 °C, which extended over the range 50–130 °C. The heat of reaction per equivalent of SiH reacted was 90–95 KJ for all three polybutadienes, which is in very good agreement with the results of Podolskii et al.[19] The samples that gave a lower heat of reaction (indicative of incomplete mixing) were rejected and the preparation was repeated.

Table IV
Critical Weight Ratios (Polybutadiene/Silane)

	calcd[a]	measd	% error
CM-1	441.8	380	−14.0
CM-3	287.5	245	−15.0
CM-5	21.3	21	−1.4

[a] Equation 6.

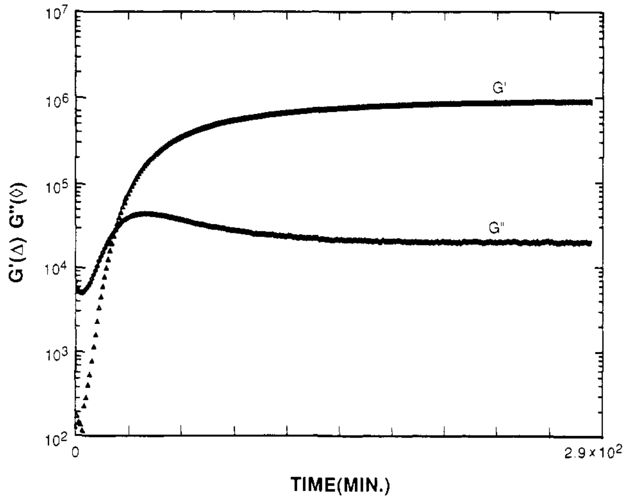


Figure 4. Development of the dynamic shear modulus during the hydrosilation reaction. The curve corresponds to CM-1, $r = 16.0$, $T_{rxn} = 60$ °C.

After the elastic measurements, portions of the samples were used to extract any soluble material, but within the range of the experimental error (less than 0.5%) the sol fraction was zero for all the samples considered. CM-5 sample was too small for soluble or elastic measurements. Since the polybutadienes CM-1 and CM-3 have a relatively high molecular weight and high functionality (about 250 and 40, respectively), just a small fraction of reacted sites per chain is enough to link the molecule to the infinite network and thus the soluble material is too low at the end of the reaction to be properly measured.

Other samples were prepared to check the critical ratio of gelation (r_c), that is, the critical stoichiometric imbalance for which gelation occurs at complete conversion. A sample was considered nongelled if it dissolved in toluene and gelled if it swelled but did not dissolve after 24 h. Using the recursive method (see Appendix), the critical weight ratio was calculated:[20]

$$w_{pbd}/w_{sil} = (M_w/M_0 - 1)M_0/(M_{sil}/2) \qquad (6)$$

where M_{sil} is the molecular weight of the cross-linker, M_0 is the molecular weight of the butadiene unit (54 g/mol), M_w is the weight-average molecular weight of the polybutadiene, and w_{pbd} and w_{sil} are the initial weight fractions of the polybutadiene and cross-linker. Table IV shows a reasonable agreement between theoretical and experimental values (note the large stoichiometric imbalances for the high molecular weight polybutadienes). As expected the agreement is better for the low molecular weight polybutadiene, since the required imbalance is not so large.

Viscoelastic Measurements. Unreacted mixtures were placed between the parallel plates of the System IV (25-mm diameter, gap = 1–2 mm), and the reaction was carried out at 60 °C under nitrogen atmosphere to avoid oxidation. The development of the

Table V
Experimental Shear Modulus and Calculated Network Parameters versus Stoichiometric Imbalance

CM-1											
r	2.620	2.623	2.655	3.137	4.123	8.710	15.97	16.00	32.0	32.11	71.33
G, MPa	2.97	3.39	2.58	2.65	1.87	1.226	0.754	0.888	0.467	0.467	0.181
νRT[a]	4.539	4.539	4.490	3.911	3.066	1.526	0.826	0.826	0.379	0.379	0.117
$2\nu/\mu$	3.96	3.96	3.96	3.96	3.93	3.86	3.78	3.78	3.60	3.60	3.32
T_e[b]	0.959	0.959	0.958	0.951	0.935	0.866	0.761	0.761	0.556	0.554	0.223
CM-3											
r	1.510	1.984	2.982	4.763	6.08	7.03					
G, MPa	2.13	1.90	1.354	0.938	0.803	0.608					
νRT[a]	2.074	1.589	1.045	0.620	0.461	0.379					
$2\nu/\mu$	3.86	3.82	3.73	3.63	3.53	3.48					
T_e[b]	0.855	0.811	0.724	0.581	0.488	0.427					
CM-1[c]											
r	0.66	0.827	0.99	1.153	1.329	1.98					
G, MPa	2.93	5.39	8.05	8.36	6.47	4.92					

[a] Calculated in MPa at $T = 60$ °C, eq A14. [b] Equation A15. [c] Additional experimental data used in Figure 10.

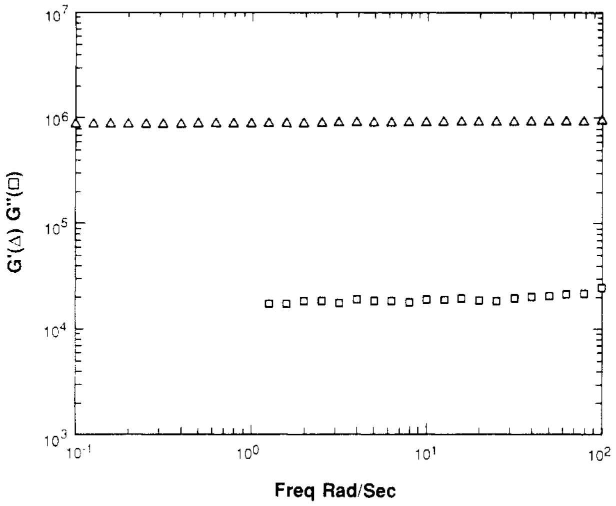


Figure 5. Frequency sweep on a reacted sample, described in Figure 4. G'' readings at low frequencies were noisy and are not shown in the figure.

Table VI
Estimation of h and G_e from the Mechanical Measurements

	h[a]	G_e, MPa[a]	G_N^0, MPa	r (corr coeff)
CM-1	0.91 ± 0.18	0.50 ± 0.27	0.70	0.969
CM-3	0.66 ± 0.37	0.96 ± 0.31	0.96	0.931

[a] 95% confidence interval was used in the calculations.

modulus was followed by using the dynamic mode, 10 rad/s, and a strain of 2–5% in order to have a sufficient torque signal (Figure 4). The runs were stopped usually after 3–5 h, when the storage modulus was considered to have reached a constant value. This was checked with a frequency sweep at 60 and 100 °C from 0.1 or 0.01 to 500 rad/s (Figure 5). For most of the samples $G'(\omega)$ did not change in more than 5–10% over the entire frequency range. For the samples made at large stoichiometric imbalance the value of the modulus at the lowest frequency (0.01 rad/s) was taken as the equilibrium value.

Some samples made from CM-1 were prepared at imbalances near the critical gel ratio. Figure 6 shows runs for samples before and after the critical gel ratio. The ungelled sample was prepared near the critical gelation ratio. It can be seen that $G''(\omega) > G'(\omega)$ and both follow approximately a power law, ω^n. At this stoichiometric imbalance (deficiency of cross-linker) the exponent was found to be $n = 0.58$, in good agreement with the conclusions of Winter et al., who experimentally found that at the gel point the exponent can change from 0.5 to 0.7 depending on the stoichiometric ratio of the reactants.[21]

Results and Discussion

Reaction Efficiency. As pointed out above the extraction of soluble material was not accurate enough for the calculation of the conversion. ^1H NMR showed no evidence of side reactions of the silane. For this reason, this kind of cross-linker seems to be more appropriate for its use as an ideal cross-linker than the siloxysilanes commonly used. Friedman et al.[17] compared the performance of different silanes for the hydrosilation of polybutadiene and showed that the networks obtained with this cross-linker have the highest modulus and almost zero extractables. Both observations suggest an efficient reaction. It also seems that no rearrangements of the double bonds in the polybutadiene chain occurred in this system. However, the reaction of internal double bonds occurred when working in excess of silanes (^{13}C NMR). Semiquantitative results obtained from ^1H NMR spectra showed that in the presence of excess vinyls the reaction of internal double bonds is less than 10%, even at $r = 1$. 1,4-Addition units definitely participate in the reaction at r lower than 1 (see Table III).

Estimation of G_e and h. To test the relation of the network structure to the modulus, some variables should be known: ν, the concentration of elastically active strands μ, the concentration of active junctions, and T_e, the trapping factor. These parameters can be calculated by using the recursive method[20,22] and knowing the progress of the reaction. Equations relating ν, μ, and T_e to conversions and chain structure are presented in the Appendix. Since with excess of vinyls no secondary reactions were observed, there was no measurable soluble material and the modulus reached a constant value, complete reaction of silane groups has been assumed for the calculations.

To check the effect of the entanglements the following form of the Langley–Graessley equation was used:

$$(G - \nu RT)/T_e = G_e - h(\mu RT)/T_e \qquad (7)$$

This form was previously used by Gottlieb, Macosko, and Lepsch[23] and by Vallês, Rost, and Macosko[24] and was also suggested by Queslel and Mark.[2] Table V shows the data used to test the model. From the plot of the data as $(G - \nu RT)/T_e$ versus $\mu RT/T_e$ (Figure 7) a slope of $(-h)$ and an intercept of G_e are expected. The results are shown in Table VI. The values of h show a low degree of suppression of the junction fluctuation. Comparison between the two networks suggests that there is more suppression of the junction fluctuations in the case of the networks formed from CM-3 than from CM-1. This could be expected from the fact that CM-3 has a larger plateau and thus the entanglement effect should be larger. Figure 7 also shows a nonzero intercept value for both polybutadienes, even considering a 95% confidence interval (Table VI). The value of G_e obtained from the CM-1

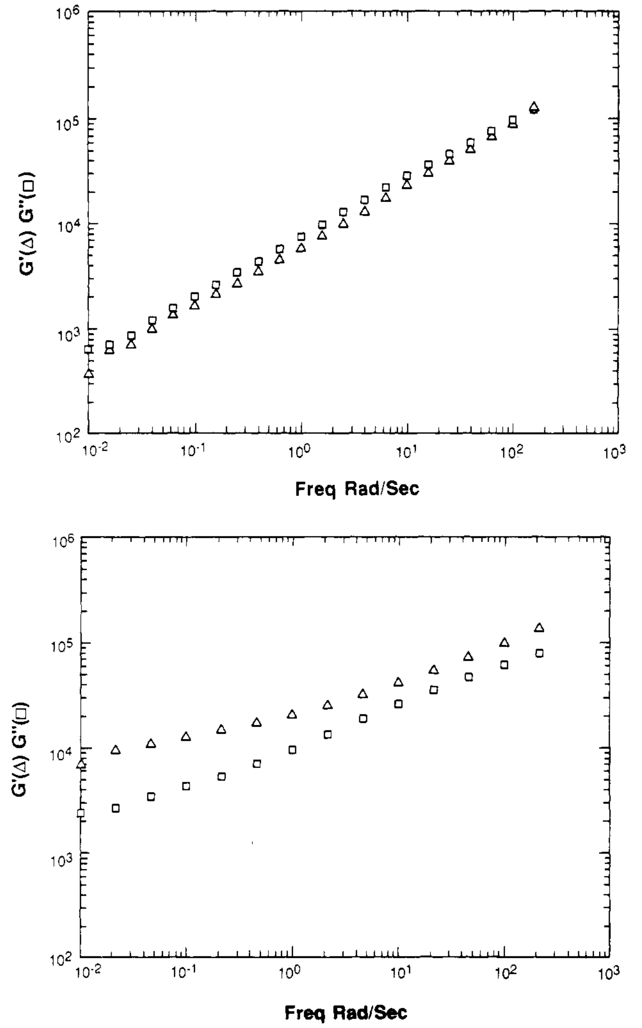


Figure 6. Frequency sweep on reacted samples of polybutadiene CM-1: (top) ungelled sample, $r = 233$, $T = 60$ °C; (bottom) gelled sample, $r = 215.1$, $T = 100$ °C.

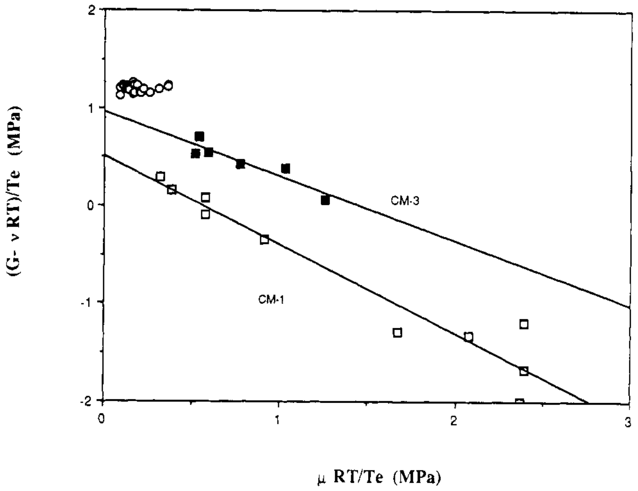


Figure 7. Test of eq 7, using CM-1 and CM-3 networks. Open squares are the results obtained from CM-1 networks, full squares are from CM-3 networks, and open circles are results from Dossin and Graessley's work.

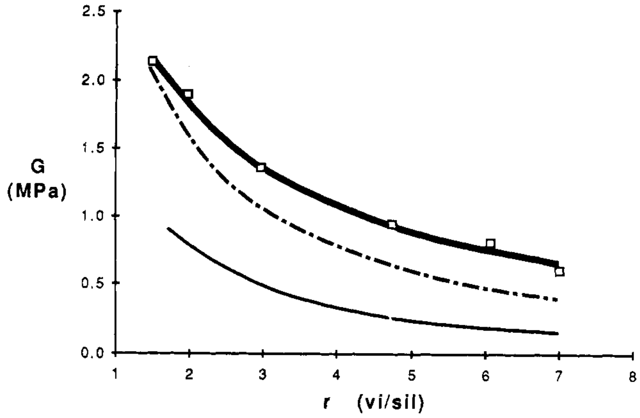


Figure 8. Comparison of the predictions of the different models with the experimental values of G for CM-3 networks. Light continuous line is predicted by using the phantom network, dashed line by using the affine model, and bold continuous line by using eq 2. Squares are experimental values.

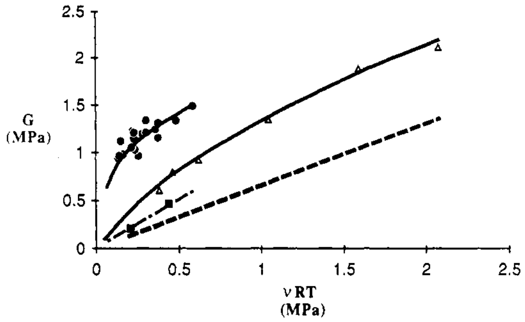


Figure 9. Comparison of the results of Dossin and Graessley[1] (circles), Brotzman and Flory[3] (squares), and CM-3 networks (triangles): (- - -) G calculated with eq 1 for CM-3 networks ($h = 0.66$); (— —) affine model ($h = 0$). The two solid lines correspond to the calculations of G by using eq 2 for the PB210 networks of ref 1 and for the CM-3 networks.

networks is lower than the measured value of the plateau modulus, but still, there is a distinguishable nonzero intercept for this system. For the CM-3 networks the value of the intercept is in very good agreement with the measured plateau for the linear polymer but is lower than the plateau measured by Dossin and Graessley in polybutadienes of similar structure (1.16 MPa).[1] The plot of G versus r in the case of CM-3 networks (Figure 8) reveals an interesting feature of this system: its modulus is everywhere higher than the prediction of the affine model, which is the upper limit for the classical theory.

Brotzman and Flory have recently reported some results obtained from polybutadiene networks cross-linked by hydrosilation.[3] They worked at large elongations and with swollen samples, thus their small deformation results are an extrapolation from large strain data. They found that their results could be explained by the use of the affine model (Figure 9). However, the polybutadienes used in their mechanical measurements are reported to be 98% cis and no indication about the percentage of vinyl is given. They also used a siloxysilane cross-linker, but no study of probable secondary reactions were reported. Thus it is difficult to compare this work to other studies. We also noted that high-cis polybutadienes have a plateau of about 0.76 MPa,[25] instead of 1.2 MPa as the authors assumed. Thus the entanglement effect should be smaller than was initially expected by Brotzman and Flory.

Dossin and Graessley worked with polybutadienes of structure similar to our CM-3 but cross-linked by irradiation.[1] They found an important contribution of the topological interactions along the contour of the chains; G_e was very close to $G_N{}^0$. They also observed a complete suppression of the junction fluctuations ($h = 0$). Figure 9 shows the calculations of G by using eq 1 and 2 with $h = 0$ and $h = 0.66$. It can be seen that Dossin and Graessley results as well as ours show an important contribution of the long-range effects of the topological interactions (G_eT_e) and that the main difference comes from the factor h in

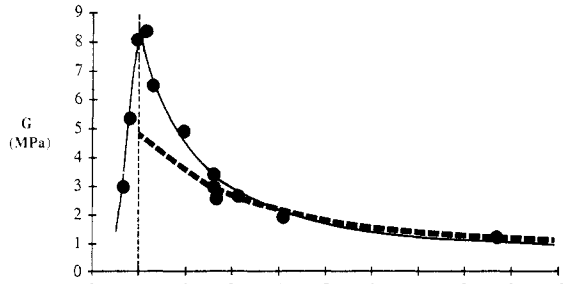


Figure 10. Modulus of CM-1 networks near $r = 1$. Points, experimental results; continuous line, an interpolation of the data; dashed line, calculated by using eq 2 and the values of h and G_e shown in Table VI.

the first term of eq 2. This could be, at least partially, due to the different "functionality" of the junctions in these two networks ($2\nu/\mu$). While in Dossin's work this value is on average equal to 4.35, in our case it is equal to 3.68. The difference between the h values could also be due to the different type of cross-linking reaction. A junction produced by irradiation will give a group of either four carbons between the primary chains (cross-linking between two vinyls) or a simple C–C bond (0.77 or 0.15 nm). A junction produced by hydrosilation will give a larger group between the polybutadiene chains of about 1.5 nm. This linking group is formed by four carbons and the cross-linker molecule. Thus hydrosilation would create a "looser" junction of higher mobility.

Highly Cross-Linked Networks. If a G versus r plot is made for the CM-1 networks (Figure 10), one can see that near $r = 1$ the theory predicts lower values than those experimentally obtained. The fact is that in this region the comparison is no longer valid. Since the starting polybutadiene has 33% reactive units, at complete conversion for $r = 1$ the length of the strands is about the same that the length of the cross-linker molecule, so the assumption of Gaussian chains is completely invalid in that region. Note also that the maximum G appears almost at $r = 1$ (experimentally $0.99 < r < 1.15$), as expected if there are no competing reactions.

Conclusions

Our results for small strain modulus can be best explained by using a network model that includes the short- and long-range effects of the topological interactions between chains. By use of two polybutadienes of different plateau modulus and the same cross-linking reaction the importance of the term G_eT_e was demonstrated. The larger the plateau modulus the greater the term G_eT_e, and as was shown, this term is essential for prediction of the modulus of CM-3, since the experimental modulus is even higher than predicted from the affine model.

The difference in the parameter h for both systems is in accord with the different importance of the entanglements on the suppression of junction fluctuations. Since the cross-linking junctions of both systems are of the same type and functionality, the suppression of mobility is larger in the networks formed from polymers of higher plateau. It also seems that tighter junctions are obtained by irradiation which would explain the complete suppression of junction fluctuations in Dossin and Graessley networks.

The ^{13}C NMR and ^{1}H NMR studies, the critical gel ratio, and the maximum modulus at $r = 1$ indicate that for the system studied, side reactions can be neglected when vinyl groups are in excess. The aromatic silane cross-linker seems to be a good candidate for further model network studies.

Appendix

In this section we just present the equations used to calculate the network parameters. Their derivation can be found in the recent works of Miller and Macosko.[20,22] The calculation is a generalization of the recursive method[26,27] applicable to the case of the cross-linking of polydisperse prepolymers with an arbitrary distribution of weight and functionality. In the present case we assumed a negative binomial distribution for the chains, as

$$P_n(L=l) = \binom{l-1}{k-1} q^k (1-q)^{l-k}, \qquad l = k, k+1, k+2, ... \tag{A1}$$

where k is the shape parameter and $1/q$ is the scale parameter. Both parameters can be calculated by knowing the number-average length of the chains (L_n) and their polydispersity ($z_p = M_w/M_n$), as

$$q = \frac{1/L_n}{z_p + 1/L_n - 1} \quad \text{and} \quad k = qL_n \tag{A2}$$

The curing of the polybutadienes was carried out by hydrosilation, which corresponds to the case of coupling through copolymerization with a small molecule. The method assumes ideal network formation (Flory–Stockmayer assumptions): (1) All functional groups of the same type are equally reactive. (2) All groups react independently of oner another. (3) No intramolecular reactions occur in finite species.

For long chains (polybutadiene) with A sites (vinyls) cross-linked through small molecules with B sites (silanes), the stoichiometric balance can be written as

$$r = \frac{E_n(F_A)/M_{nA}}{2/M_B} \frac{w_A}{w_B} \tag{A3}$$

where w_A is the proportion of mass corresponding to the polybutadiene chains and $w_B = 1 - w_A$, M_{nA} is the number-average molecular weight of the initial polybutadiene chains, M_B is the molecular weight of the cross-linker (monodisperse), $E_n(F_A)$ is the expected functionality of the polybutadiene chains picked by number, $E_n(F_A) = pL_n$ for the chosen distribution, and p is the fraction of reactive units in the long chains and it is assumed independent of the length of the chain.

The key quantity needed for the calculation of postgel parameters is $P(F_A^{\text{out}})$, the probability of "seeing" finite mass when "looking out" from an A site. In this case $P(F_A^{\text{out}})$ is the solution of

$$P(F_A^{\text{out}}) = 1 - r\alpha^2 + r\alpha^2 \Phi_{F-1,s}[P(F_A^{\text{out}})] \tag{A4}$$

where

$$\Phi_{F-1,s}(z) = \frac{q^{k+1}(1-p+pz)^{k-1}}{[1-(1-q)(1-p+pz)]^{k+1}} \tag{A5}$$

is the probability generating function of the site distribution of $F_A - 1$ and α is the conversion of A groups. Only one of the roots of the eq A4 has physical meaning, being equal to 1 before the gelation and a number between 0 and 1 after that point. The conversion at which gelation occurs is the limit between those two behaviors and for the case of a monodisperse bifunctional cross-linker is equal to

$$[\alpha\alpha_B]_c = [E_s(F_A) - 1]^{-1} \tag{A6}$$

where α_B is the conversion of B groups. When working in excess of B groups ($r = \alpha_B/\alpha < 1$), eq A6 can be written as

$$\alpha_c = [r(E_s(F_A) - 1)]^{-1/2} \tag{A7}$$

which is a generalization of previous works.[26,27] To calculate the critical ratio (in excess of A groups) at which gelation does not occur we can rewrite eq A6 as

$$\alpha_B^2/r = [E_s(F_A) - 1]^{-1}$$

and taking $\alpha_B = 1$ we will get

$$r = E_s(F_A) - 1 \tag{A8}$$

where $E_s(F_A) = pM_{wA}/M_0 + 1 - p$ and M_0 is the weight of the repeating unit. Replacing r by its definition (eq A3) and using the expression for $E_s(F_A)$ we can get the critical ratio expressed as a weight ratio of the initial reactants (eq 6).

Other quantities are needed to calculate the concentration of junction points or the concentration of elastically effective strands. These are the probabilities that there are 0, 1, or 2 paths to the infinite network from a randomly chosen repeat unit along the chain ($g_R(i)$, $i = 0, 1,$ or 2). Thus

$$g_R(0) = \Phi_{F-1,s}[P(F_A^{out})]$$

$$g_R(1) = 2\left\{\frac{1 - \Phi_{F,n}[P(F_A^{out})]}{[1 - P(F_A^{out})]E_n(F_A)} - \Phi_{F-1,s}[P(F_A^{out})]\right\}$$

$$g_R(2) = 1 - g_R(0) - g_R(1) \tag{A9}$$

where

$$\Phi_{F,n}(z) = \left[\frac{q(1 - p + pz)}{1 - (1 - q)(1 - p + pz)}\right]^k \tag{A10}$$

is the probability generating function of the number distribution of F_A.

Then the concentration of elastically active junctions μ can be calculated as

$$\mu = \rho_{pbd}w_B/M_B\{1 - [P(F_B^{out})]^2 - 2r\alpha P(F_B^{out}) \times [g_R(1) + g_R(2)] - [r\alpha g_R(1)]^2\} \tag{A11}$$

where we add the factor ρ_{pbd} to the expression in ref 22 to obtain the number of junctions per unit of volume. The density of the polybutadiene used in this expression is[11]

$$\rho_{pbd} = \rho_0 \exp[-0.75 \times 10^{-3}(T - T_0)], \quad \rho_0 = 0.895 \text{ g/cm}^3 \text{ at } 25\ ^\circ\text{C} \tag{A12}$$

$P(F_B^{out})$ is analogous to $P(F_A^{out})$ but "looking out" from a B site (silane):

$$P(F_B^{out}) = 1 - r\alpha + r\alpha g_R(0) \tag{A13}$$

The concentration of elastically active chains is

$$\nu = \rho_{pbd}w_B/(2M_B)\{[g_R(1) + 2g_R(2)]2r\alpha[1 - P(F_B^{out})] - 2[r\alpha g_R(1)]^2\} \tag{A14}$$

and the trapping factor is

$$T_e = [g_R(2)]^2 \tag{A15}$$

As mentioned before the complete derivation of these equations and other network parameters can be found in ref 20 and 22.

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Registry No. (Butadiene)(*p*-bis(dimethylsilyl)benzene) (copolymer), 114532-82-0; *p*-bis(dimethylsilyl)benzene, 2488-01-9; 2-hexene, 592-43-8; 1,4-hexadiene, 592-45-0.

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