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Elastic Behavior of *cis*-1,4-Polybutadiene

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ABSTRACT: This study presents uniaxial extension measurements on *cis*-1,4-polybutadiene networks of known junction functionality. The observed values of the reduced force from uniaxial extension measurements conform to the constrained junction theory of Flory. The reduced force intercept at $1/\alpha = 0$ is fully comprehensible in terms of the cycle rank of the network and can be calculated from chemical considerations. This holds even though the polybutadiene melt has a high-plateau modulus. Therefore, discrete topological entanglements do not contribute perceptibly to the equilibrium modulus of polybutadiene networks.

Introduction

The reduced stress in uniaxial extension is defined by

$$[f^*] = f^*(V/V^0)^{-1/3}(\alpha - \alpha^{-2})^{-1} \qquad (1)$$

where f^* is the tensile force per unit area in the reference state, V^0 is the volume of the reference state, V is the system volume at measurement, and α is the extension ratio relative to the length of the sample when isotropic at the same volume V. The reduced force is a convenient measure of the elastic response of a polymer network to an applied stress. According to earlier theories, $[f^*]$ should be constant.[1] In fact, it generally decreases markedly with elongation. Recent theory reformulates $[f^*]$ of a real polymer network as[2-5]

$$[f^*] = [f_{ph}^*](1 + f_c/f_{ph}) \qquad (2)$$

where f_{ph} represents the force which would be exerted by a topologically equivalent phantom network, f_c is the contribution of the force from the effects of constraints on the fluctuations of network junctions, and $[f_{ph}^*]$ is the reduced force for the equivalent phantom network (i.e., a hypothetical network devoid of material properties; its constituent chains can transect one another, no chain excludes others from the volume it occupies, and the fluctuations of cross-links are constrained only by the chains attached directly to it). The reduced force for a perfect phantom network is given, according to theory,[3,6] by

$$[f_{ph}^*] = \xi kT/V^0 = (\phi - 2)\mu_J/2V^0 \qquad (3)$$

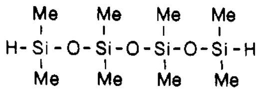
where ξ is the cycle rank of the network, μ_J the number of network junctions, and ϕ the junction functionality. The ratio f_c/f_{ph} depends on two parameters κ and ζ; κ is of primary importance and is defined as the ratio of the mean-square radius of the fluctuations of the junctions in the phantom network to the mean-square radius of the Gaussian domain of constraint in the undistorted network, while the secondary parameter ζ is empirical and may reflect inhomogeneities of the network topology. It is given by eq 43 in ref 4. In the limit of high extension and/or dilution, f_c/f_{ph} vanishes according to this theory.

Thus elastic behavior in the limit of high extension and/or dilution is fully comprehensible from a consideration of the covalent structure of the network. Equation 3 implicitly excludes contributions to the reduced force from discrete entanglements[3] of one network chain with another. If a contribution should be included for permanently "trapped entanglements" of this nature, as is often contended to be necessary, their contribution would be reflected in apparent values of ξ, or of μ_J, exceeding those deduced from the chemical constitution of the network alone. Some authors have attempted to ascribe such contributions to the plateau modulus of the un-cross-linked polymer melt.[7,8] Equilibrium swelling data provide additional confirmation of the relationship between the reduced force of a phantom network and the cycle rank density determined from chemical considerations. Theoretical treatment of swelling data in the phantom network limits yields[9-11]

$$(\xi/V^0) = -[\ln(1 - v_{2,s}) + v_{2,s} + \chi v_{2,s}^{\;2}](v_{2,s}^{\;-1/3}/V_1) \qquad (4)$$

where $v_{2,s}$ is the volume fraction of polymer at swelling equilibrium, χ is the polymer–solvent interaction parameter, and V_1 is the molar volume of the diluent.

This study presents uniaxial extension measurements on *cis*-1,4-polybutadiene (PBD) networks of known junction functionality. Primary PBD chains were cross-linked by a hydrosilylation reaction between the PBD double bonds and 1,1,3,3,5,5,7,7-octamethyltetrasiloxane (OMTS)



$$\mathrm{H{-}\underset{Me}{\overset{Me}{Si}}{-}O{-}\underset{Me}{\overset{Me}{Si}}{-}O{-}\underset{Me}{\overset{Me}{Si}}{-}O{-}\underset{Me}{\overset{Me}{Si}}{-}H}$$

to produce a network that contains tetrafunctional junctions. The value of $[f_{ph}^*]$ determined from uniaxial extension measurements is compared with the stoichiometric value calculated from eq 3. The polybutadiene melt has a high-plateau modulus (1.2 MPa)[12] and thus provides a model system well suited for assessment of whether or not discrete topological entanglements contribute to the equilibrium modulus of an elastomer network.

Previous investigators have studied PBD networks formed by the action of free radicals induced photochemically, by peroxide, or by high-energy radiation. In a dicumyl peroxide charged system, Van der Hoff[13] estimated the cross-linking efficiency to be approximately 12 for each

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Table I

polymer	M_w × 10^{-3}	M_w/ M_n	mol % OMTS/ monomer $10^2(\rho/2)$	exptl % gel	expected from theory	
					Flory	Langley
A	358	2.5	0.535	97.6	99.9	99.9
B	414	2.1	0.263	100.0	99.8	99.8
C	345	1.9	0.253	99.8	99.7	99.7
D-1	350	2.1	1.50	100.0	100.0	100.0
D-2*	350	2.1	0.0119	47.0	44.7	40.8
D-3	350	2.1	0.160	97.3	99.3	99.0
CDS-B-4*	24.7	1.1	0.423	81.0	85.6	94.7

pair of free radicals released by the peroxide in an antioxidant-free material. Infrared analysis showed that free radical propagation proceeds via the unsaturated double bonds in both the main chain (1,4) and in vinyl side groups (1,2), a process denoted "cross-polymerization". Thus, the polybutadienyl radical, once initiated, is capable of successively joining double bonds in neighboring polymer chains. Large junctions of high functionality (with $\phi > 20$ in some instances) may be formed through cross-polymerization in this manner. Other investigators[14,15] have studied the peroxide cross-linking of PBD by measuring the sol–gel ratio of a series of samples charged with varying amounts of dicumyl peroxide. They concluded that the free radicals have large kinetic chain lengths (3–8) which result in network junctions of 4–8 functionality. Through the intervention of chain transfer the functionality of these junctions may be somewhat less than the kinetic chain length of the radical. In any event, the structures of networks formed through the action of free radicals are difficult to quantify.

Experimental Section

Solvents. Reagent grade toluene and 95% ethanol were used for fractionation without further purification. Spectroscopic grade benzene was used as the solvent in sample-deposition solutions. Inasmuch as the OMTS reacts rapidly with moisture, all traces of water should be removed from the benzene prior to its use for this purpose. To this end, the benzene used for dissolution of samples C, CDS-B-4, D-1, D-2, and D-3 was first refluxed over calcium hydride and distilled to remove any residual water. A less stringent procedure in which the benzene was not redistilled was employed for samples A and B.

Benzene, practical grade decane, and hexadecane (Aldrich, 99%) were used as swelling diluents. The density of hexadecane is calculated to be 0.7866 g/cm^3 at 33.6 °C.[16]

Polymer. The PBD used in the stress–strain measurements and for one of the samples in the sol–gel study (see below) was Goodyear Budene 1207, having a cis-1,4 content of 98%. The samples were prepared for cross-linking by fractionation from a 2–2.5% toluene solution using ethanol as the precipitant. Throughout this and subsequent dissolution procedures an antioxidant (*p*-benzoquinone) concentration of approximately 0.05% was maintained. The goal of fractionation was to confine somewhat the molecular weight distribution of PBD; narrow fractions were not desired. Four batches of polymer were fractionated; the molecular weight characteristics of each were determined by size exclusion chromatography (Waters Model 150C liq/gel permeation chromatograph with a refractive index detector) and are given in Table I. After fractionation, the polymer was dried under vacuum and stored in the dark at 0 °C.

The second sample for the sol–gel study (see below) was prepared from Goodyear batch no. CDS-B-4 polybutadiene. This polymer was a weight-average molecular weight of 24 700, a polydispersity index of 1.1, and a microstructure of 40% cis-1,4, 52% trans-1,4, and 8% vinyl-1,2. It was used without further purification.

PBD, the cross-linking agent OMTS (Petrach Systems) at the concentrations given in Table I, and 1.0–1.5 ppm of a platinum catalyst (chloroplatinic acid, Petrach Systems) were dissolved in benzene. The solution was deposited in a Teflon mold having a rectangular cavity ca. 4.0 × 4.0 × 0.5 cm^3 and equipped with a removable Teflon plate to facilitate sample removal. Solution deposition and all procedures which follow were conducted under a flowing dry nitrogen atmosphere at room temperature. After thorough evaporation of solvent, a section of the sample was dissolved in toluene to check for incipient gelation; in no case was evidence of gelation detected. In a drybox, the sample was transferred to a stainless steel mold (ca. 4.0 × 4.0 × 0.05 cm^3) which was placed between two stainless steel plates covered with Teflon sheets. This assembly was wrapped in a plastic bag containing desiccant and pressed to obtain uniform samples with thicknesses of 0.03–0.05 cm. The samples were allowed to relax in the mold for 4 days prior to the execution of cross-linking in bulk at 140 °C for 3 h through hydrosilylation[17] of PBD double bonds. It was imperative to exclude all water from the sample to prevent the hydrolysis[18] of OMTS.

The cross-linked sheets were extracted with toluene for 30 h at room temperature. The gel remaining after soluble constituents were removed was weighed, and the percentages of gel are given in Table I. Exercise of extreme care was necessary during the filtration of the supernatant of samples D-2 and CDS-B-4 used in gelation measurements. Toluene was gradually removed by deswelling with solutions of increasing ethanol concentration. Drying was completed by subjecting the samples to a vacuum for 24 h at room temperature. Visually the swelling of the gels was uniform, indicating good cross-linking uniformity and little if any residual orientation from the molding process.

The specific volume of PBD at 33.6 °C interpolated from the data of Barlow,[19] 1.1216 cm^3/g, was used for reducing the measured masses to volume fractions. The density of OMTS is reported to be 0.8632 at 20 °C.[17]

Swelling Measurements. Equilibrium degrees of swelling in benzene, decane, and hexadecane were determined at 35 °C on rectangular specimens (ca. 0.3 × 0.5 cm^2). Changes in the linear dimensions (unswollen vs. swollen) of two sides of the specimen were measured with a cathetometer and averaged.

Mechanical Measurements. Rectangular specimens of ca. 3 cm in length were cut with a stainless steel die. The cross section of each specimen (ca. 0.3–0.6 × 0.03–0.05 cm^2) was measured with a cathetometer (precision of ±0.001 cm). The samples were mounted in lightweight grips ca. 2.5 cm apart; the lower grip was equipped with a hook for holding weights, and the upper one was attached to a load cell (Straindyne Engineering Co. Model CFT12-70GR) situated above the chamber. The load cell was mounted on a temperature-controlled block maintained at 35 °C. Calibration of the cell verified that the relationship between applied stress and output voltage was linear throughout our experimental range. Reference marks were provided by two lengths of thin wire inserted near the extremities of the measurement area (ca. 0.3 cm apart). In order to minimize damage to the sample, they were inserted while the specimen was swollen. A load was applied, and the distance between the wires was measured at periodic intervals until the sample was judged to be at equilibrium (see below). The weight was then increased or decreased and a new equilibrium point was established. Data obtained during loading and unloading cycles showed no significant differences.

Stress–strain measurements on unswollen samples and those partially swollen with hexadecane were carried out at 33.6 °C. Samples swollen to equilibrium in decane were submerged in the liquid (plus 0.05% antioxidant) in a cylindrical container at 35 °C. Partially swollen samples were prepared by immersing specimens in the diluent for a limited time and allowing 48 h for uniform distribution of the diluent throughout the specimen. The amount of diluent was determined by weighing and the volume fraction of polymer calculated from the known specific volumes of polymer and liquid, additivity of volumes being assumed.

Although equilibration during stress–strain measurements was fairly rapid for swollen samples, a period of 2 h was allowed for attainment of equilibrium after each load. However, the question of whether equilibrium was established for bulk specimens is difficult to answer. Several bulk samples subjected to a uniaxial stress continued to relax after 6 days. In our experiments a quasi-steady-state reading was taken after 48 h.

Results

Gelation. The cross-linking of polybutadiene is analogous to random condensation of bifunctional diene units with ϕ-functional units. The following development is a review of classical gelation theory[20] and assumes the following: the primary PBD chains may be approximated by a most probable distribution; all functional groups are chemically equivalent; the reactivity of a given diene unit is independent of the size or structure of the molecule to which it is attached; and intramolecular cross-linking reactions may be neglected. In support of the first assumption, we note that the ratios M_w/M_n given in Table I approximate two as the most probable distribution. The departures, therefore, should not vitiate the following analysis significantly. Accordingly, we take the probability that a given functional group of a branch unit leads via a chain of bifunctional units to another branch unit to be

$$\alpha_b = p\rho/[1 - p(1 - \rho)] \qquad (5)$$

where ρ is the cross-linking density defined as the ratio of interlinked units to the total number of diene units and p corresponds to the extent of reaction in the analogous polycondensation. Thus, $1 - p$ is the probability of the occurrence of an end of a primary molecule. For a most probable distribution of primary chain lengths, whose weight- and number-average degrees of polymerization are $\bar{y}_w$ and $\bar{y}_n$, respectively, p is given by $1 - 2/(\bar{y}_w + 1) = 1 - 1/\bar{y}_n$. The critical condition for incipience of infinite networks is

$$\alpha_b{}^c = 1/(\phi - 1) \qquad (6)$$

The foregoing relations and those that follow should apply to the networks of higher functionality ϕ formed by cross-polymerization as well as to those with $\phi = 4$ formed by cross-linking pairs of units.

Using the complexity distribution approach[20] and assuming that the proportion of ϕ-functional units is small ($\rho \ll 1$), one obtains for the weight fraction of polymer containing n branch units

$$w_n = (1 - \alpha_b)^2[2(\phi n - n + 1)/\phi]w_n'\beta^n \qquad n \geq 0 \quad (7)$$

with

$$w_n' = (\phi(\phi n - n)!)/((\phi n - 2n + 2)!n!) \qquad (8)$$

$$\beta = \alpha_b(1 - \alpha_b)^{\phi-2} \qquad (9)$$

Summation of the weight fractions of all finite species according to eq 7 gives unity for $\alpha_b < \alpha_b{}^c$. When $\alpha_b > \alpha_b{}^c$, the weight fraction sol is

$$w_s = \sum_{n=0}^{\infty} w_n = (1 - \alpha_b)^2/(1 - \alpha_b')^2 \qquad (10)$$

where α_b' is the lower root of eq 9. The weight fraction gel is

$$w_g = 1 - (1 - \alpha_b)^2/(1 - \alpha_b')^2 \qquad (11)$$

For the random interlinking of primary chains having a most probable distribution, the corresponding definition of p may be substituted into eq 5 to yield

$$\rho = 2\alpha_b/(1 - \alpha_b)(\bar{y}_w - 1) = \alpha_b/(1 - \alpha_b)(\bar{y}_n - 1) \qquad (12)$$

Once the cross-linking density for a given α_b and $\bar{y}_w$ or $\bar{y}_n$ is obtained, the partitioning of cross-linked units between sol and gel in a ϕ-functional system is given by

$$\rho' = \rho w_s{}^{(\phi-2)/2}(1 + (\phi/2)\rho[1 - w_s{}^{(\phi-2)/2}]) \qquad (13)$$

for the sol and

$$\rho'' = \rho(1 - w_s)^{-1}(1 - w_s{}^{\phi/2}[1 + (\phi/2)\rho(1 - w_s{}^{(\phi-2)/2})]) \qquad (14)$$

for the gel.

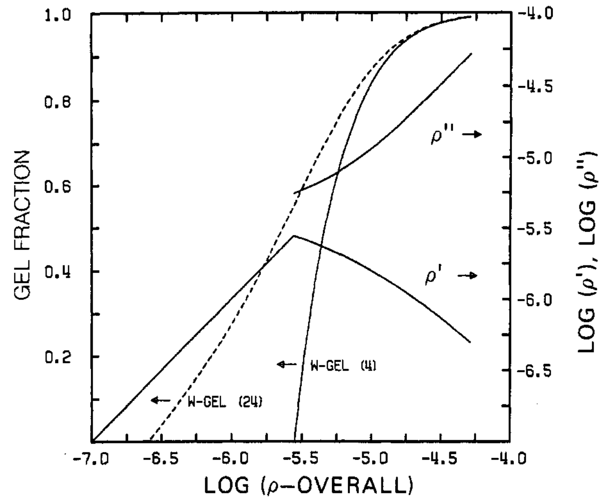

Figure 1. Gel fraction and distribution of cross-link density between sol and gel vs. the log of the total cross-link density for the cross-polymerization of the primary chains having a most probable distribution. Two curves representing networks with junction functionalities of 4 (solid) and 24 (dashed) are shown with arrows pointing to the left. In each case $M_w = 358000$. The other solid lines represent the gelation behavior of a tetrafunctional system and have arrows pointing to the right.

Calculations pertaining to interlinking of primary molecules through introduction of junctions with functionalities $\phi = 4$ and 24 are shown in Figure 1, where the weight fraction gel and the densities ρ' and ρ'' of cross-linked units in the sol and gel, respectively, are plotted against the overall cross-link density ρ. The solid lines represent the designated tetrafunctional behavior while the dashed line indicates the percent gel in a system containing junctions of 24-functionality. The difference in cross-link density between networks of tetra- and 24-functionality at a given fraction of gel is greatest at low gel fractions. However, this difference persists even at 90% gelation, where it is approximately 10%. Although these results illustrate the consequence of cross-linking primary chains having a most probable distribution (with $M_w = 358000$), the following analysis is general and elucidates the gelation behavior of all cross-linking systems with regard to the functionality of the junctions that are formed.

The effect of functionality on the gelation characteristics of a network are clearly illustrated in Figure 1. While distinctions between networks of differing junction functionality become less (in the gelation sense) at higher gel fractions, the effect of junction functionality on the equilibrium mechanical properties of a network are significant, as this study demonstrates.

Cross-Linking Efficiency. The efficiency of the process of cross-linking with OMTS was tested by comparing observed weight fractions w_g of gel with those calculated according to Flory (given above) and Langley[21] theories. The theoretical values from Flory's theory for the weight fraction of gel were determined by substituting the $\bar{y}_w$ and ρ values from Table I into eq 12 to give α_b and using this result in eq 9 to obtain α_b'; α_b and α_b' were then substituted into eq 11. The results from Langley's theory were obtained by using eq 29 of ref 21 with $p = 0$. All the values of percent gel are given in Table I. When the steep slope of the curve for tetrafunctional networks in Figure 1, the experimental uncertainties, and the order of magnitude differences in molecular weight of the un-cross-linked polymers used to prepare samples D-2 and CDS-B-4 are considered, the agreement between experiment and theory indicates that cross-linking is quantitative to within 10–15%.

Table II[a]

figure	sample	v_2	κ	$[f^*]/RT \times 10^4$ $1/\alpha = 0$	$[f^*]/RT \times 10^4$ $1/\alpha = 1$
2	A	0.256	0.46	0.680	0.693
3	B	0.191	5.06	0.320	0.359
4	C	0.800	*b*	0.395	0.725
		0.539	6.84		0.551
		0.339	6.16		0.497
		0.186	5.92		0.469
6	D-3	0.920	*b*	0.241	0.419
		0.739	6.73		0.358
		0.411	4.82		0.300
		0.155	3.99		0.266

[a] $\zeta = 0$ for all fits. [b] The κ values selected as best fits to the data in the least-squares sense are abnormally high. This, plus the knowledge that a wide range of κ values, lower in magnitude, could have been used to fit the data equally well, undermines the relevance of these κ values.

Table III

sample	diluent	$v_{2,\mathrm{eqm}}$	χ	$(\xi/V^0) \times 10^4$, mol/cm^3
A	benzene	0.0995	0.253[a]	0.680[a]
	decane	0.256	0.477[a]	
B	benzene	0.0679	0.275[a]	0.320[a]
	decane	0.191	0.477[a]	
C	benzene	0.0800	0.292	0.395
	decane	0.186	0.445	
	hexadecane	0.304	0.545	
D-1	benzene	0.236		2.47
	decane	0.422		
	hexadecane	0.492		
D-3	benzene	0.0588	0.280	0.241
	decane	0.155	0.453	
	hexadecane	0.256	0.538	

[a] The values were determined by using the cycle rank density deduced from elasticity measurements (see text).

Stress-Strain Measurements. The stress-strain isotherms at 33.6 °C for PBD networks of varying interjunction chain molecular weight are given in Figures 2–6. In each figure the reduced force is plotted vs. $1/\alpha$ with the solid lines representing the best theoretical fits in the least-square sense to the experimental isotherms. The parameters used to calculate these theoretical lines are given in Table II. The lower dashed lines represent the cycle rank density calculated from the chemical constitution with the correction due to dangling chain ends included. This correction is given by[22]

$$(\xi/V^0)_{\mathrm{corrected}} = (\xi/V^0)_{\mathrm{chemical}} - 1/(M_{\mathrm{n}} v_{\mathrm{sp}}) \qquad (15)$$

where v_{sp} is the specific volume of PBD and the cycle rank density from chemical considerations is calculated from eq 3. The upper dashed lines represent the affine limit for a perfect network obtained with respect to the corrected chemical value. The polymer volume fraction of the sample is given next to each isotherm.

Stress–strain measurements, obtained for samples swollen to equilibrium with decane, have been corrected for the effect on the stress of the small increase in swelling with extension;[23] the values of χ given in Table III were employed in making this correction. No correction was required for samples swollen with hexadecane because it is a nonvolatile solvent.

Figures 2 and 3 contain data for networks A and B, respectively. In each case the reduced force for samples swollen with decane (triangles) fall below the value determined from "the chemistry" of each system by 21 and 25%. The apparent chemical value is the reduced force intercept of the theoretical fit to stress–strain data at $1/\alpha = 0$; this was used in Table III to calculate the starred values. In both figures bulk data are given by +; these data may not be true equilibrium data due to long relaxation times and the onset of strain-induced crystallization, which was observed to occur in bulk samples at higher elongations. Strain-induced crystallization was not observed for any of the samples swollen with diluent.

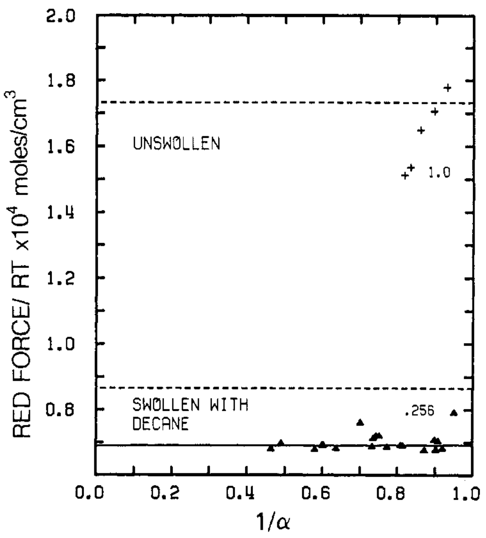

Figure 2. Reduced force as functions of α^{-1} for network A. Data for bulk samples (+) and samples swollen with decane (▲) are given, and the polymer volume fractions are indicated with each isotherm. The solid curves were calculated according to theory with parameters given in Table III. The lower dashed line represents the cycle rank density calculated from the chemical constitution of network A with corrections due to dangling chain ends included. The upper dashed line represents the affine limit for a perfect network obtained with respect to the corrected chemical value of network A.

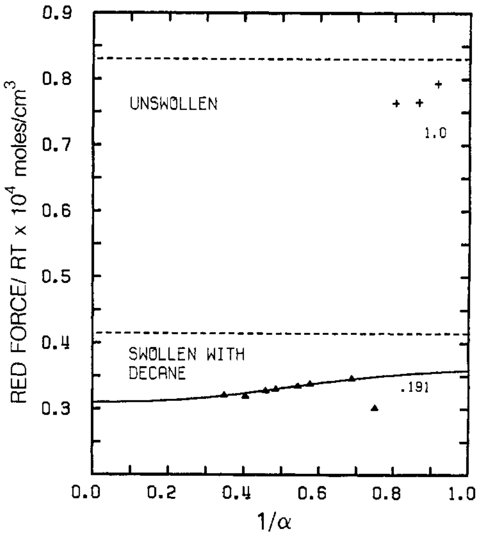

Figure 3. Same as Figure 2 but for network B.

In considering the discrepancy between experiment and theory for networks A and B, the effect of water during sample preparation became a concern. To correct this problem, the benzene was further purified (see Experimental Section) and all mixing and deposition procedures occurred under a dry nitrogen atmosphere. The result of this modification to the experimental procedure is embodied in the strain–strain isotherms of networks C, D-1, and D-3 in Figures 4–6. The lower portions of Figures 4 and 6 contain data for bulk sample (C only) and samples swollen to equilibrium with decane; the upper portions contain data for samples swollen to varying degrees with hexadecane. All the theoretical curves were generated with

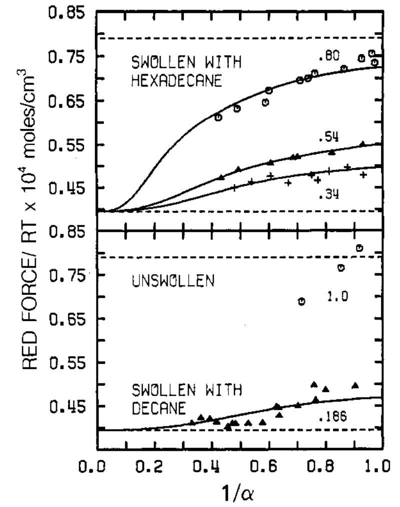

Figure 4. Data for network C. The lower portion presents data for bulk samples (○) and samples swollen with decane (▲) while the upper portion contains data for samples swollen to varying degrees with hexadecane. The polymer volume fractions are indicated with each set of data, and dashed lines are as indicated in Figure 2.

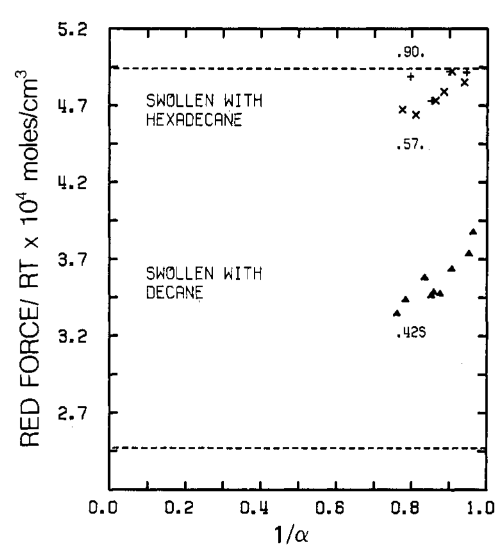

Figure 5. Same as Figure 2 but for network D-1.

the cycle rank density from chemical data. There is good agreement between experiment and theory. Samples A and B are therefore deemed to be somewhat inferior because the cycle rank deduced for elastic measurements is more reliable owing to inefficiency of "the chemistry" due to the presence of water in the deposition solvent.

Equilibrium stress–strain data on bulk samples were difficult to obtain because of the aforementioned problems. Therefore, the behavior of PBD networks in which the fluctuations of the junctions are highly constrained was explored with network D-1, which is highly cross-linked. Although the junctions in highly cross-linked networks are subject to smaller relative constraint from entanglements, these junctions will remain highly constrained. Measurements on samples swollen with hexadecane eliminate the problem of equilibrium and provide a measure of this limit; the experimental data exhibit large departures from phantom behavior. But these departures are within the framework of the theory; network D-1 exhibits affine-like behavior.

Swelling. The polymer volume fractions at swelling equilibrium at 35 °C are given in Table III. The χ values have been calculated from the cycle rank density ξ as determined from the molar ratios of OMTS; eq 4 is used for this purpose under the assumption that the swollen network conforms to the phantom limit. This is a valid assumption. The χ for sample D-1 was not determined since its mean interjunction chain molecular weight, 1800, is too low to validate the Gaussian approximation. The footnoted values for samples A and B were determined by using the cycle rank density deduced from elasticity measurements. An examination of the apparent χ values reveals that those for benzene are more sensitive to the cycle rank density than the corresponding values for decane. Even so, for each diluent the χ values for the networks agree within experimental error. The χ values for the PBD and benzene system are contrasted with previously reported values of 0.325[24] (unspecified PBD microstructure) and 0.21[25] (98% cis-1,4 and ca. 34% cis-1,4, 54% trans-1,4, 12% vinyl-1,2) obtained by vapor sorption techniques. From Table III the mean χ values for benzene, decane, and hexadecane are respectively 0.265, 0.463, and 0.542.

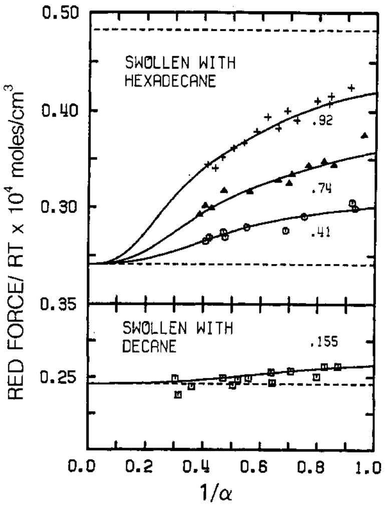

Figure 6. Same as Figure 4 but for network D-3.

Discussion and Conclusions

The results of this study are in difference with those from previous investigators. Mark[26] has reported stress–strain isotherms of networks prepared using peroxide, sulfur, and high-energy radiation. The reduced force behavior of these networks was compared in terms of the ratio of linear-fit parameters ($2C_2/2C_1 = R$) derived from $[f^*] = 2C_1 + 2C_2\alpha^{-1}$. Although this technique of fitting data linearly has now been thoroughly discredited,[2-6] it did provide a means of examining earlier work. The R values for peroxide- (0.35 ± 0.15) and radiation- (1.69 ± 0.2) cross-linked networks are compared with that of the sulfur- (1.30 ± 0.2) cross-linked networks. The low value of R for peroxide-cross-linked networks is comprehensible if junctions are considered to be of high functionality. If $2C_2$ were a reflection of network inhomogeneities, the higher value of R for radiation-cross-linked networks is explicable by a spatially nonrandom distribution of junctions of high functionality. This conclusion has support from the nonequality of interjunction chain molecular weights deduced from swelling and elasticity measurements.[26,27]

Dossin and Graessley[7] (D–G) have examined polybutadiene networks in which cross-linking was induced by high-energy radiation. Their networks were assumed to be tetrafunctional; according to their analysis junction fluctuations were deemed to be completely suppressed. This is precisely the expected effect of junctions of high functionality. The fluctuations of these junctions are small and ineffectual in reducing the stress below that expected for an affine network. Recently, Colby et al.[28] gave calorimetric evidence that PBD with a microstructure studied by D–G has a T_m near −26 °C that is insensitive to chain length. But the birefringence results of Mark and Llorente[29] (M–L) demonstrate that this polymer (ca. 50% cis-1,4 and 50% trans-1,4) could have crystallites persisting "up to temperatures well above 60 °C" and they are likely to exist in the unstretched state; the experiments of D–G were conducted at 25 °C. Birefringence measurements are more sensitive to small extents of molecular orientation and the existence of microcrystallites than DSC measurements. Thus orientation may occur in a strained PBD network of mixed microstructure as a result of adjacent chains, each with several sequential trans units, forming microcrystallites. The protracted relaxation of stress reported by D–G, from 1 to 30 days being required for equilibrium, also suggests the presence of crystalline aggregates. D–G reported reduced force values from elasticity measurements that were 2.5–6.5 times that from chemical considerations. D–G attribute this apparent increase of 0.294×10^{-4} to 0.397×10^{-4} mol/cm^3 in the ξ/V^0 of their networks above the chemical value to permanently "trapped entanglements" in the network topology. In comparison, the ξ/V^0 of our samples, as determined by chemical and mechanical measurements, are given in Table III and are of comparable magnitude to the alleged entanglement contributions. M–L observed that swelling their networks with decalin decreased their reduced force measurements by 6-fold. The presence of a diluent evidently suppressed crystallization or facilitated the attainment of true equilibrium or both.

In the determination of the equilibrium elastic properties of polymer networks subject to the effects of strain-induced crystallization and/or long equilibration times, it is important that bulk measurements be compared with similar tests conducted on samples swollen with a diluent. In general, the diluent both suppresses crystallization and facilitates the attainment of equilibrium.

Recently, Macoska and Saam[30] demonstrated that side reactions consume approximately 25% of the SiH without forming end-links in the hydrosilylation cure of polyisobutene. This estimate of reaction inefficiencies is certainly large when the low sol fractions reported in Table I for the samples subjected to uniaxial deformations and the agreement between experiment and theory in our gelation study are considered. Also, the procedure employed to fit theory to experimental stress–strain data may easily be modified to account for reaction inefficiencies of 10% with little effect on the parameters given in Table II.[31] In any event, the modulus should be reduced below the value expected from chemical considerations by the degree of reaction inefficiency—purportedly 25% in this instance. Dossin and Graessley[7] reported the contribution to the modulus from "topologically trapped" entanglements to be between 50% and 150% greater than that deduced from the covalent structures of our network. The expected contribution to the equilibrium modulus from trapped entanglements is so great that the existence of small reaction inefficiencies in the cross-linking reaction will not alter the following conclusions.

Previous studies on PBD networks, which were reputed to be well-characterized, are therefore vitiated by the nonquantitative chemistry of the networks and the effect of strain-induced crystallization. Departures from theory cannot be attributed to the highly speculative contributions from interchain entanglements. PBD of high cis-1,4 content is free from the problems of crystallization at our experimental conditions,[27,29] and gelation studies establish that the chemistry of our system is approximately quantitative. The elastic behavior of well-characterized polybutadiene networks conforms to the constrained junction theory. At large extension (and/or high dilution) phantom network behavior is approached. The reduced-force intercept at $\alpha^{-1} = 0$ is fully comprehensible in terms of the cycle rank of the network and can in fact be calculated from the chemical constitution. Discrete topological entanglements therefore do not contribute perceptibly to the equilibrium modulus of polybutadiene networks.

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