microstructures but not for others. The excess temperature dependence appears to depend on a thermally activated process rather than the free volume process that governs viscosity for linear polymers. The activation energies were used to estimate activation coefficients for the various species. A rough connection was established between these values and the temperature coefficient of chain dimensions for the species. For the saturated polymers, corresponding in microstructure to copolymers of ethylene, there appears to be a systematic relationship with the mole fraction of counit. The results are in general accord with expectations based on the difference in relaxation mechanisms available to entangled linear and branched polymers.

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Registry No. Polyisoprene (homopolymer), 9003-31-0; polybutadiene (homopolymer), 9003-17-2.

References and Notes

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Examination of the Critical Parameters in the Constrained Junction Theory of Rubber Elasticity

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ABSTRACT: Stress–strain data previously obtained for a wide variety of unswollen and swollen polymer networks in elongation are interpreted by using the Flory–Erman theory of rubber elasticity. The interpretation is carried out as objectively as possible, with theoretical curves chosen on the basis of minimum residuals between theory and experiment and with realistic estimates of the uncertainties involved. High-elongation values of the reduced stress obtained from the theoretical curves were found to be very nearly independent of the degree of swelling. They differed significantly, in some cases, from the intercepts ($2C_1$) obtained by simple linear extrapolations of the data. Low-elongation values, however, are quite close to the linearly extrapolated values. In the theory employed, the reduced stress depends on the extent to which junction fluctuations are constrained, which in turn depends on the degree of interpenetration of the chain configurational domains. Values of an interpenetration parameter, although defined to account for the configurational characteristics of the chains investigated, were unfortunately found to show some dependence on the degree of swelling and the nature of the elastomeric chains.

Introduction

The most general molecular theory of rubber elasticity treats both "phantom" networks (in which the chains can transect one another and cross-links can fluctuate freely) and real networks (in which chain entangling constrains these fluctuations).[1-3] It has been used with considerable success in interpreting stress–strain measurements, in particular the elongation dependence of the reduced stress defined by

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

where f^* is the tensile force per unit area in the reference

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Table I
Characteristics of the Polymers

polymer	repeat unit	M_0[a]	l^2,[b] Å^2	d, g cm^{-3}	$\langle r^2\rangle_0/nl^2$[c]
poly(dimethylsiloxane)	$-[Si(CH_3)_2O-]$	37.1	2.69	0.970	7.8
cis-1,4-polybutadiene	$-[CHCHCH_2CH_2-]$	13.5	2.20	0.903	4.9
polyisobutylene	$-[C(CH_3)_2CH_2-]$	28.1	2.34	0.915	6.5
poly(oxyethylene)	$-[(CH_2)_2O-]$	14.7	2.14	1.10	5.2
poly(oxypropylene)	$-[CH(CH_3)CH_2O-]$	19.4	2.14	0.998	5.0
poly(tetramethylene oxide)	$-[(CH_2)_4O-]$	14.4	2.22	0.982	6.1
poly(ϵ-caprolactone)	$-[(CH_2)_5COO-]$	16.3	2.22	1.09	6.1
poly(ethyl acrylate)	$-[CH_2CHCOOC_5H_5-]$	50.1	2.34	1.09	8.5
poly(dimethoxyphosphazene)	$-[P(OCH_3)_2N-]$	53.5	2.43	1.44	10[d]
poly(phenoxy(*p*-ethylphenoxy)phosphazene)	$-[P(OC_6H_5)(OC_6H_4C_2H_5)N-]$	129.6	2.43	1.26	32

[a] Molecular weight per skeletal bond. [b] Mean-square skeletal bond length. [c] Characteristic ratio, where $\langle r^2\rangle_0$ is the unperturbed dimensions and n the number of skeletal bonds. [d] Arbitrary estimate.

state, V° 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 stress for a phantom network equivalent to a real network under investigation would be

$$[f^*]_{ph} = \xi kT/V^\circ \qquad (2)$$

where ξ is the cycle rank of the network. In real networks there is a contribution f_c to the force that arises from network chain constraints on the cross-link fluctuations. It is a function of ξ, the cross-link functionality ϕ, the severity of the constraints κ, and the degree of nonaffineness in the strain-induced attenuation of the constraints ζ.[2,3] Thus, for a real network

$$[f^*] = [f^*]_{ph}(1 + f_c/f_{ph}) \qquad (3)$$

where f_{ph} represents the force that would be exerted by a topologically equivalent phantom network measured under identical conditions.

The parameter κ depends on the degree of chain interpenetration and may be written[3]

$$\kappa = I[N_a d\langle r^2\rangle_0/M_0]^{3/2}(kT/[f^*]_{ph})^{1/2}[(\phi - 2)/\phi]^{3/2}[2/(\phi - 2)] \qquad (4)$$

where I is a proportionality constant, N_a Avogadro's number, d the density, $\langle r^2\rangle_0$ the mean-square unperturbed dimensions of the chains, M_0 their molecular weight per skeletal bond, k the Boltzmann constant, and T the absolute temperature. Deletion of the functionality dependence permits definition of an interpenetration parameter

$$J \equiv \kappa[M_0/N_a d l^2 C_\infty]^{3/2}([f^*]_{ph}/kT)^{1/2} \qquad (5)$$

in which C_∞ is the characteristic ratio $\langle r^2\rangle_0/nl^2$ in the limit of large n, where n is the number of chain skeletal bonds, and l^2 is their mean-square length.

The present study was undertaken to interpret stress–strain isotherms in elongation reported by one of the present authors for a wide variety of elastomeric networks. The primary goal is characterization of possible trends in κ and J with changes in the chemical nature of the elastomer, its cross-link functionality, degree of cross-linking, and degree of swelling.

Preparation and Some Characteristics of the Networks

The polymers used to prepare the elastomer networks were poly(dimethylsiloxane) (PDMS), *cis*-1,4-polybutadiene (PBD), polyisobutylene (PIB), poly(oxyethylene) (POE), poly(oxypropylene) (POP), poly(tetramethylene oxide) (PTMO), poly(ϵ-caprolactone) (PCL), poly(ethyl acrylate) (PEA), poly(dimethoxyphosphazene) (PDMP), and poly(phenoxy(*p*-ethylphenoxy)phosphazene) (PPEP). Their chemical structures and some of their other relevant characteristics are given in Table I.

Two series of PDMS networks were prepared, the first[4] by γ irradiation and the second[5] by end-linking reactive chains. The polymer used in the first series had a molecular weight of approximately 0.5 × 10^6 and, to facilitate cross-linking, had unsaturated groups present to the extent of 0.5 mol% $-Si(CH_3)(CH{=}CH_2)O-$ repeat units. Three portions were given γ radiation doses of 0.90, 0.77, and 0.63 Mrad. Extractions of the resulting tetrafunctional networks gave sol fractions of 0.117, 0.125, and 0.134, respectively. The swelling diluent used (during the elasticity measurements) was a linear dimethylsiloxane fluid having a degree of polymerization of approximately 160. The second series was prepared from a sample of PDMS having a number-average molecular weight, M_n, of 11.3 × 10^3 and vinyl groups at both ends of at least 95% of the chains. Cross-link functionalities ranging from 3 to 11 were obtained (with partially successful attempt at $\phi = 37$) by end-linking the chains with multifunctional silanes. Sol fractions were in the range 0.033–0.061.

The PBD sample employed was of high molecular weight and was at least 94% cis-1,4 in stereochemical structure.[6] The network PBD-S was cross-linked with 1 wt % sulfur at 150 °C for 2 h and was assumed to have a cross-link functionality of 4. The diluent used to swell it was 1,2,4-trichlorobenzene. The second network, PBD-G, was cross-linked by γ radiation, under vacuum and at room temperature, to a dose of 11.2 Mrads. Network PBD-P was cross-linked by using 1 wt % benzoyl peroxide at 120 °C for 1 h. Because of the likelihood of free-radical polymerization of the double bonds in the latter two networks,[7,8] their cross-link functionality is not reliably known, and values of both 4 and 24 were adopted.[8] The swelling diluent for the two networks was 1,2-dichlorobenzene.

Three PIB networks were prepared from mixtures of butyl rubber with suitable curing agents, primarily disulfides.[9] Variation in the mol % unsaturation in the polymer and in the amount of curing agents was used to obtain different degrees of cross-linking. The reactions were carried out at 150 °C, under vacuum, for 1 h. The tetrafunctional networks thus prepared had sol fractions that ranged from 0.085 to 0.138. The swelling diluent employed was 1,2,4-trichlorobenzene.

Four POE networks were obtained by end-linking hydroxyl-terminated chains having values of M_n of 0.880 × 10^3, 1.46 × 10^3, 3.25 × 10^3, and 6.82 × 10^3.[10] The end-linking agent was an aromatic triisocyanate ($\phi = 3$), and the reactions were carried out under vacuum at 95 °C for 50 h. Sol fractions ranged from 0.031 to 0.067, and the swelling diluent was phenylacetate. The same reaction was used to prepare four POP networks from atactic chains having values of M_n of 0.800 × 10^3, 0.920 × 10^3, 1.98 × 10^3, and 3.70×10^3,[11] a single PTMO network with $M_n = 0.880 \times 10^3$,[10] and four PCL networks with $M_n = 0.570 \times 10^3$, 0.910×10^3, 1.31×10^3, and 1.95×10^3.[12] Sol fractions were in the range 0.001–0.040.

The PEA sample employed was atactic and had a molecular weight of approximately 2.9×10^6.[13] It was cross-linked into four tetrafunctional networks by using γ-radiation doses of 5.0–48 Mrad.

Two tetrafunctional phosphazene networks were prepared from high molecular weight samples of PDMP and PPEP by using γ radiation.[14] The doses employed were 24.7 and 17.6 Mrad, respectively, and the sol fractions were 0.08 and 0.16, respectively.

Stress–Strain Measurements

Stress–strain isotherms had been obtained on the extracted networks in elongation at the temperatures and degrees of swelling specified in columns 3 and 4 of Table II. Measurements had been conducted in a way permitting elastic equilibrium to be approached as closely as possible. Details are given in the original publications.[4–6,9–14] Excluded from consideration here were results obtained at elongations sufficiently high to cause increases in stress from strain-induced crystallization or limited chain extensibility.

Data Treatment

The objective of this study is not only to determine the best theoretical fit to a given reduced-force isotherm, but also to include realistic estimates of the experimental error inherent in each isotherm. A family of reduced-force isotherms is generated via eq 3 and 43 of ref 2 for each data set by fixing the values of $[f^*]_{ph}$, ζ, and ϕ (determined by the chemistry of the system) and varying κ. Each curve within this family is scrutizinized by summing the squared differences between the theoretical and experimental reduced force values and dividing this sum by the number of points comprising the reduced-force isotherm; this result is the mean residual of error (MRE). The curve within this family that minimizes the MRE is selected as the best fit with respect to κ for a given value of $[f^*]_{ph}$ (MRE-κ). In a stepwise fashion, $[f^*]_{ph}$ is varied (ζ and ϕ remain constant), and the entire minimization procedure is repeated; a series of MRE-κ curves is generated. From this series of curves (MRE-κ), which represent a range in $[f^*]_{ph}$, the curve with the smallest MRE is chosen as the best fit to the experimental isotherm (BF-MRE). The values of ζ, $[f^*]_{ph}$, and κ for the BF-MRE curves are listed in Table II. The best-fit parameters and the polymer characteristics (Table I) are used to calculate J from eq 5; the values of J are listed in Table II.

For each network the values of $[f^*]_{ph}$ and J at different degrees of swelling are averaged; these average parameter values when $\zeta = 0$ are given in Table III. An average value of J for each polymer at all degrees of cross-linking and swelling is determined and given in this table.

We acknowledge two sources of error: the average value of $[f^*]_{ph}$ for a given network may vary by approximately ±5%, and an individual datum point may vary by 10%. The latter condition is examined by changing one datum point by plus 10% of its value and following the above procedure to determine the mean residual of the modified isotherm with respect to the theoretical curve generated by using the parameters reported in Table II. This procedure is repeated by sequentially changing each datum point in the isotherm by first plus 10% and then minus 10% of its value. The resulting residuals are averaged, and an acceptable range of residual values is established as those between this averaged value and that of the minimum residual value (BF-MRE) generated by using the best-fit parameters given in Table II. The former error condition is utilized by determining those values of κ for each $[f^*]_{ph}$ value within ±5% of the average $[f^*]_{ph}$ value, which generates a residual within the acceptable residual range; the corresponding J values were also determined.

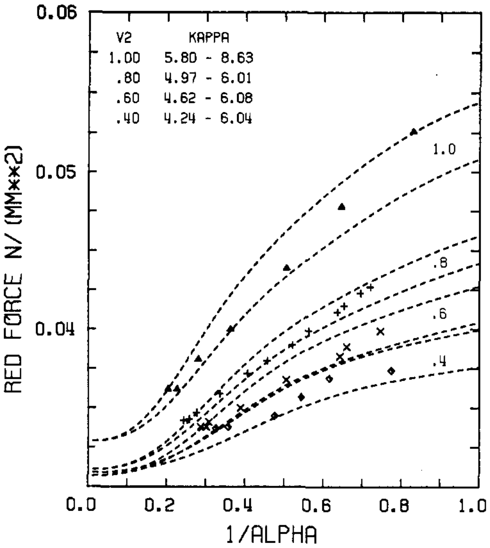

Figure 1. Reduced force as functions of α^{-1} for PDMS swollen to varying degrees with a linear dimethylsiloxane. The points represent experimental results of Chiu and Mark[4] for specimens of their sample irradiated with 0.90 Mrad and swollen to the extents indicated by the values of the volume fraction to the right of each isotherm and also in the inset in the upper left of this figure. The dashed curves were calculated according to theory with $\zeta = 0.0$ and κ values given in the inset.

For each reduced-force isotherm, we objectively determined the range in $[f^*]_{ph}$ with accompanying κ values that yield J values close to the average polymer J values given in Table III. The parameter ranges identified by this criterion are listed in Table IV and termed best parameter values.

Each curve in representative Figures 1–7 is generated by selecting the $[f^*]_{ph}$ value from the best parameter values (Table IV, column 6) that is closest to the averaged $[f^*]_{ph}$ value (Table IV, column 4); these $[f^*]_{ph}$ values are listed in column 4 of Table V. The dotted lines in each figure represent the theoretical curves generated by using the extrema in acceptable κ values for the chosen value of $[f^*]_{ph}$.

Discussion of Results

Figures 1–3 illustrate the effect of ζ on the theoretical description of the PDMS data in the first data grouping in our tables. For each dilution, the $\zeta = 0$ curves given in Figure 1 represent the data better than the curves for higher ζ. For each dilution the data fall within the dotted curves generated from the extremes in κ as indicated in each figure. In Figures 2 and 3 ζ increases, the resultant theoretical representations become increasingly sigmoidal, and reasonable fits to the data cannot be obtained throughout the dilution range. A similar ζ dependence is seen for the PBD-S data in Figures 4 and 5; at the higher ζ value, the theoretical curves become sigmoidal at low dilution and fits to the data become poor. The same ζ behavior is seen in each system examined by this study. Therefore, the best results are achieved for $\zeta = 0$; Table V contains these results.

Figures 1, 4, 6, and 7 give the $\zeta = 0$ curves and experimental data for PDMS*, PBD-S*, PIB*, and POE*, respectively. (The asterisk superscript designates which

Table II
Experimental Variables and Parameters for the Best-Fit Isotherms

polymer	ϕ^a	T, °C	v_2^b	ζ^c	$[f^*]_{ph}$,^{d} N mm^{-2}	κ^e	J^f
PDMS*^{g}	4	30	1.00	0.00	0.0325	7.66	0.112
			0.80	0.00	0.0317	4.79	0.0693
			0.60	0.00	0.0317	4.10	0.0594
			0.40	0.00	0.0318	3.96	0.0575
			1.00	0.05	0.0355	6.75	0.104
			0.80	0.05	0.0334	4.91	0.0730
			0.60	0.05	0.0330	5.02	0.0742
			0.40	0.05	0.0333	4.69	0.0697
			1.00	0.10	0.0366	6.94	0.108
			0.80	0.10	0.0341	6.09	0.0915
			0.60	0.10	0.0335	7.72	0.115
			0.40	0.10	0.0343	9.96	0.150
PDMS	4	30	1.00	0.00	0.0245	14.3	0.182
			0.80	0.00	0.0238	4.74	0.0644
			0.60	0.00	0.0232	4.63	0.0574
			0.40	0.00	0.0221	4.35	0.0526
PDMS	4	30	1.00	0.00	0.0146	15.3	0.150
			0.80	0.00	0.0139	8.23	0.0790
			0.60	0.00	0.0129	10.8	0.100
			0.40	0.00	0.0130	4.77	0.0443
PDMS	3	25	1.00	0.00	0.158	3.37	0.110
	4		1.00	0.00	0.188	4.32	0.154
	4.6		1.00	0.00	0.176	17.9	0.614
	6		1.00	0.00	0.228	6.87	0.269
	8		1.00	0.00	0.269	2.64	0.113
	11		1.00	0.00	0.292	1.87	0.0829
	37		1.00	0.00	0.230	9.34	0.368
PBD-S*^{h}	4	25	1.00	0.00	0.222	7.93	0.203
			0.80	0.00	0.213	6.43	0.162
			0.60	0.00	0.204	6.74	0.166
			0.40	0.00	0.192	8.07	0.193
			0.20	0.00	0.212	5.21	0.130
			1.00	0.05	0.245	6.83	0.184
			0.80	0.05	0.232	6.04	0.158
			0.60	0.05	0.227	5.47	0.142
			0.40	0.05	0.219	7.68	0.196
			0.20	0.05	0.231	12.0	0.313
			1.00	0.10	0.250	10.3	0.280
			0.80	0.10	0.237	7.77	0.206
			0.60	0.10	0.232	8.12	0.213
			0.40	0.10	0.229	25.0	0.651
			0.20	0.10	0.240	4.81	0.128
PBD-G^i	4	10	1.00	0.00	0.107	20.2	0.368
			0.80	0.00	0.097	16.4	0.285
			0.60	0.00	0.098	9.77	0.171
			0.40	0.00	0.093	8.11	0.138
			0.20	0.00	0.093	6.78	0.116
	24	10	1.00	0.00	0.162	24.0	0.541
			0.80	0.00	0.135	20.0	0.411
			0.60	0.00	0.127	22.8	0.455
			0.40	0.00	0.111	27.2	0.508
			0.20	0.00	0.101	29.7	0.528
PBD-P^j	4	10	1.00	0.00	0.147	2.96	0.0619
			0.80	0.00	0.143	2.16	0.0446
			0.60	0.00	0.142	1.42	0.0291
			0.40	0.00	0.142	0.84	0.0172
			0.20	0.00	0.140	1.07	0.0218
	24	10	1.00	0.00	0.164	18.2	0.401
			0.80	0.00	0.153	16.1	0.343
			0.60	0.00	0.143	17.7	0.364
			0.40	0.00	0.138	25.4	0.514
			0.20	0.00	0.136	23.0	0.462
PIB	4	30	1.00	0.00	0.082	10.0	0.274
			0.80	0.00	0.083	2.44	0.0668
			0.60	0.00	0.073	3.98	0.102
			0.40	0.00	0.070	2.65	0.0664
PIB*	4	20	1.00	0.00	0.166	3.22	0.127
			0.80	0.00	0.104	3.74	0.116
			0.60	0.00	0.104	2.75	0.0856
			0.40	0.00	0.095	3.14	0.0934
PIB	4	15	1.00	0.00	0.131	3.95	0.138
			0.80	0.00	0.123	4.11	0.140
			0.60	0.00	0.119	2.16	0.0725
			0.401	0.00	0.107	1.21	0.0385
POE	3	25	1.00	0.00	0.721	1.14	0.0423

Table II (Continued)

polymer	ϕ[a]	T, °C	v_2[b]	ζ[c]	$[f^*]_{ph}$,[d] N mm^{-2}	κ[e]	J[f]
			0.597	0.00	0.637	1.58	0.0550
POE	3	25	0.565	0.00	0.549	2.26	0.0735
			0.488	0.00	0.337	14.8	0.376
			0.390	0.00	0.608	1.56	0.0531
POE*	3	25	0.429	0.00	0.260	1.76	0.0393
			0.325	0.00	0.240	2.52	0.0543
			0.220	0.00	0.259	0.960	0.0214
POE	3	25	0.457	0.00	0.275	3.41	0.0785
			0.341	0.00	0.345	1.19	0.0307
			0.291	0.00	0.314	1.29	0.0317
POP	3	25	1.00	0.00	1.25	0.39	0.035
POP	3	25	1.00	0.00	1.12	0.67	0.0577
POP	3	25	1.00	0.00	0.538	3.16	0.188
POP	3	25	1.00	0.00	0.248	2.17	0.0881
PTMO	3	25	1.00	0.00	0.691	1.83	0.0571
PCL	3	25	1.000	0.00	2.21	2.81	0.162
			0.775	0.00	2.63	1.68	0.105
			0.558	0.00	3.11	0.80	0.0547
PCL	3	25	1.000	0.00	2.27	0.41	0.0239
			0.853	0.00	2.16	0.60	0.0357
			0.459	0.00	2.25	0.42	0.0244
PCL	3	25	1.000	0.00	1.34	2.48	0.111
			0.766	0.00	1.21	4.76	0.202
			0.394	0.00	0.97	13.4	0.512
PCL	3	25	1.000	0.00	0.88	4.91	0.178
			0.623	0.00	0.83	9.38	0.363
			0.450	0.00	0.84	11.4	0.439
			0.402	0.00	0.85	11.8	0.428
PEA	4	25	1.00	0.00	0.075	5.05	0.161
PEA	4	25	1.00	0.00	0.055	6.47	0.176
PEA	4	25	1.00	0.00	0.043	10.0	0.241
PEA	4	25	1.00	0.00	0.044	6.83	0.167
PEA	4	25	1.00	0.00	0.031	15.6	0.319
PDMP	4	30	1.00	0.00	0.069	6.47	0.106
PPEP	41	30	1.00	0.00	0.013	8.30	0.0477

[a] Cross-link functionality. [b] Volume fraction of polymer present in the network. [c] Parameter characterizing deformation of domains of constraint. [d] Reduced stress in the limit at high elongation. [e] Measure of entanglement constraints. [f] Interpenetration coefficient. [g] Asterisks in this and the following tables specify results shown graphically in the figures. [h] Sulfur cured. [i] γ radiation cured. [j] Peroxide cured.

Table III
Values of $[f^*]_{ph}$ Averaged over Degrees of Swelling and Values of J Averaged over Degrees of Swelling and Degrees of Cross-Linking[a]

polymer	ϕ	T, °C	$[f^*]_{ph}$, N mm^{-2}	J
PDMS*	4	30	0.0320 ± 0.0004	0.0746 ± 0.0255
PDMS	4	30	0.0234 ± 0.0010	0.0891 ± 0.0621
PDMS	4	30	0.0136 ± 0.0008	0.0933 ± 0.0442
				0.0857 ± 0.0098[b]
PBD-S*	4	25	0.209 ± 0.011	0.171 ± 0.029
PBD-G	4	25	0.098 ± 0.006	0.216 ± 0.107
	24	25	0.127 ± 0.024	0.489 ± 0.054
PBD-P	4	25	0.143 ± 0.003	0.0349 ± 0.0183
	24	25	0.147 ± 0.012	0.417 ± 0.071
PIB	4	30	0.077 ± 0.006	0.127 ± 0.099
PIB*	4	20	0.117 ± 0.033	0.106 ± 0.019
PIB	4	15	0.120 ± 0.010	0.0973 ± 0.050[b]
				0.110 ± 0.015
POE	3	25	0.679 ± 0.059	0.0487 ± 0.0090
POE	3	25	0.498 ± 0.143	0.167 ± 0.181
POE*	3	25	0.253 ± 0.011	0.0383 ± 0.016
POE	3	25	0.311 ± 0.035	0.0470 ± 0.0273
				0.0753 ± 0.0613[b]
POP	3	25		0.0922 ± 0.0675
PCL	3	25	2.65 ± 0.45	0.145 ± 0.72
PCL	3	25	2.23 ± 0.06	0.0377 ± 0.0090
PCL	3	25	1.17 ± 0.19	0.371 ± 0.282
PCL	3	25	0.85 ± 0.02	0.485 ± 0.172
				0.260 ± 0.204[b]
PEA	4	25		0.213 ± 0.067

[a] Parameter ζ = 0.0. [b] Average J value for this polymer, at all degrees of cross-linking and swelling.

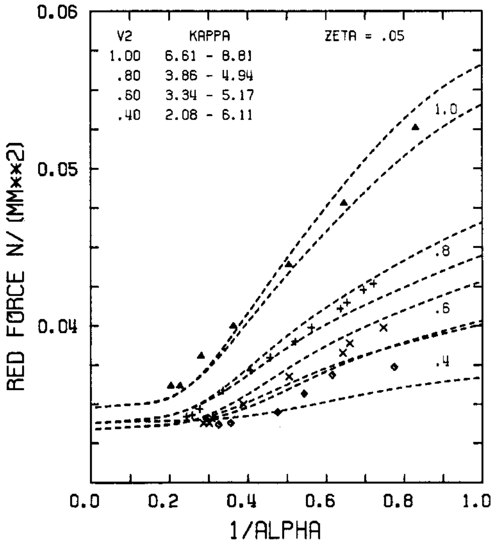

Figure 2. Same as Figure 1 but with ζ = 0.05.

system within the same polymer grouping is graphed; see tables.) For each system, the chosen intercept of the reduced force at high elongation, $[f^*]_{ph}$, and the averaged value of the low-extension intercepts, generated by using the extreme values of κ, are listed in columns 4 and 7 of Table V, respectively. These intercept values are compared with those obtained by using the linear Mooney–Rivlin (M–R) equation of the reduced force, $[f^*] = 2C_1 + 2C_2\alpha^{-1}$. The high- and low-extension M–R intercepts are given in columns 5 and 8 of Table V, and these intercepts, normalized by the corresponding theoretical intercept, are given in columns 6 and 9 of the same table. Absence of a high-elongation $[f^*]_{ph}$ value for a particular isotherm means that theoretical parameters could not be found

Table IV
Some Averaged Results and the Theoretical Parameters Giving the Best Fits of These Results

		averaged results			best values of parameters		
polymer	ϕ	v_2	$[f^*]_{ph}$, N mm^{-2}	J	$[f^*]_{ph}$, N mm^{-2}	κ	J
PDMS*	4	1.00	0.0320	0.0856	0.0329–0.0336	5.80–5.76	0.0856
		0.80			0.0304–0.0311	6.03–6.01	0.0856
		0.60			0.0304–0.0307	6.03–6.01	0.0856
		0.40			0.0304–0.0309	6.01–5.97	0.0856
PDMS	4	1.00	0.0234	0.0856	0.0246	11.39	0.145
		0.80			0.0225–0.0234	7.02–6.86	0.0856
		0.60			0.0222	6.99	0.0849
		0.40			0.0222	5.60	0.0679
PDMS	4	1.00	0.0136	0.0856	0.0143	15.55	0.151
		0.80			0.0135–0.0140	9.07–8.86	0.0856
		0.60			0.0131–0.0133	9.08–9.16	0.0856
		0.40			0.0129	6.20	0.0573
PDMS	3	1.00	0.158	0.110	0.156–0.162	3.40–3.33	0.110
	4	1.00	0.188	0.154	0.185–0.191	4.36–4.29	0.154
	4.6	1.00	0.176	0.614	0.173–0.178	18.0–17.7	0.614
	6	1.00	0.228	0.269	0.224–0.230	6.93–6.84	0.269
	8	1.00	0.269	0.113	0.266–0.272	2.66–2.63	0.113
	11	1.00	0.292	0.0829	0.289–0.295	1.88–1.86	0.0829
	37	1.00	0.230	0.368	0.228–0.232	9.38–9.32	0.368
PBD-S*	4	1.00	0.209	0.171	0.219	7.82	0.199
		0.80			0.209–0.215	6.85–6.76	0.171
		0.60			0.199–0.206	7.03–6.91	0.171
		0.40			0.199–0.206	7.03–6.91	0.171
		0.20			0.202–0.207	6.98–6.90	0.171
PBD-G	4	1.00	0.0988	0.216	0.103	25.4	0.456
		0.80			0.100–0.103	12.2–12.0	0.216
		0.60			0.093–0.097	12.7–12.4	0.216
		0.40			0.093	9.42	0.161
		0.20			0.093	8.03	0.137
	24	1.00	0.127	0.489			
		0.80			0.132–0.133	24.0	0.489
		0.60			0.122–0.128	25.0–24.5	0.489
		0.40					
		0.20					
PBD-P	4	1.00	0.143	0.0349	0.150	2.05	0.0431
		0.80			0.144–0.149	1.69–1.66	0.0349
		0.60			0.137–0.142	1.74–1.70	0.0349
		0.40			0.136	1.74	0.0349
		0.20			0.136–0.142	1.73–1.70	0.0349
	24	1.0	0.147	0.417			
		0.80			0.149–0.154	19.9–19.5	0.417
		0.60			0.140–0.145	20.5–20.1	0.417
		0.40			0.140–0.142	20.4–20.3	0.417
		0.20					
PIB	4	1.00	0.075	0.101	0.079	9.77	0.261
		0.80			0.079	3.78	0.101
		0.60			0.072–0.075	3.96–3.87	0.101
		0.40			0.071	2.81	0.0707
PIB*	4	1.00	0.105	0.101	0.110	4.24	0.136
		0.80			0.103–0.108	3.26–3.17	0.101
		0.60			0.100–0.103	3.29–3.25	0.101
		0.40			0.100	2.19	0.0668
PIB	4	1.00	0.124	0.101	0.130	3.27	0.115
		0.80			0.125–0.130	2.92–2.88	0.101
		0.60			0.113–0.118	3.07–3.03	0.101
		0.40			0.112	0.87	0.0283
POE	3	1.000	0.679	0.0473	0.691–0.713	1.30–1.28	0.0473
		0.597			0.645–0.669	1.35–1.32	0.0473
POE	3	0.565	0.579	0.0473	0.589–0.608	1.41–1.39	0.0473
		0.488			0.597–0.608	1.40–1.39	0.0743
		0.390			0.605–0.608	1.39	0.0473
POE*	3	0.429	0.250	0.0473	0.250–0.255	2.16–2.14	0.0473
		0.325			0.0242–0.249	2.20–2.16	0.0473
		0.220			0.237–0.244	2.22–2.19	0.0473
POE	3	0.457	0.330	0.0473	0.313	1.78	0.0439
		0.341			0.323–0.334	1.90–1.87	0.0473
		0.291			0.313	1.63	0.0400
POP	3	1.00	1.25	0.0355	1.23–1.27	0.391–0.384	0.0355
POP	3	1.00	1.12	0.0577	1.10–1.14	0.674–0.665	0.0577
POP	3	1.00	0.538	0.188	0.532–0.546	3.16–3.11	0.188
POP	3	1.00	0.248	0.0881	0.244–0.252	2.19–2.16	0.0881
PTMO	3	1.00	0.691	0.0571	0.678–0.700	1.86–1.84	0.0574
PCL	3	1.000	2.65	0.277	2.52	1.88	0.156
		0.775			2.52	2.21	0.183

Table IV (Continued)

		averaged results			best values of parameters		
polymer	ϕ	v_2	$[f^*]_{ph}$, N mm^{-2}	J	$[f^*]_{ph}$, N mm^{-2}	κ	J
		0.558			2.52	3.04	0.251
PCL	3	1.000	2.23	0.277	2.12	0.83	0.0630
		0.853			2.12	0.83	0.0630
		0.459			2.12	1.08	0.0819
PCL	3	1.000	1.17	0.277	1.15	4.53	0.253
		0.766			1.18–1.23	4.89–4.79	0.277
		0.394			1.23	5.63	0.325
PCL	3	1.000	0.85	0.277	0.831–0.852	5.82–5.75	0.277
		0.623			0.893	7.53	0.371
		0.450			0.893	9.20	0.453
		0.402			0.893	9.72	0.479
PEA	4	1.00	0.075	0.161	0.071–0.076	5.20–5.03	0.161
PEA	4	1.00	0.055	0.176	0.052–0.055	6.66–6.55	0.176
PEA	4	1.00	0.043	0.241	0.041–0.043	10.2–9.99	0.241
PEA	4	1.00	0.044	0.167	0.042–0.044	7.00–6.83	0.167
PEA	4	1.00	0.031	0.319	0.029–0.031	16.2–15.6	0.319
PDMP	4	1.00	0.069	0.106	0.067–0.072	6.57–6.36	0.106
PPEP	4	1.00	0.013	0.0477	0.013	8.33	0.0477

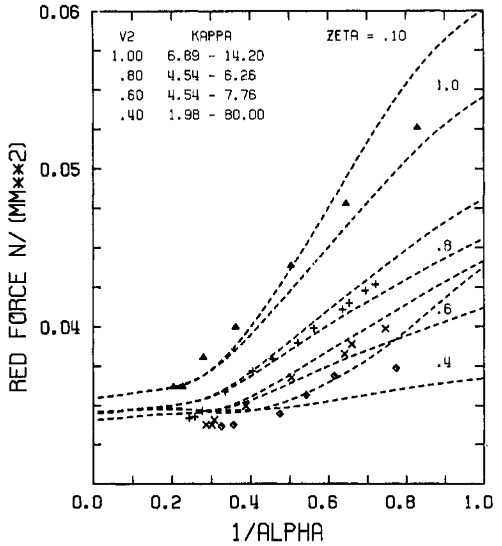

Figure 3. Same as Figure 1 but with $\zeta = 0.10$.

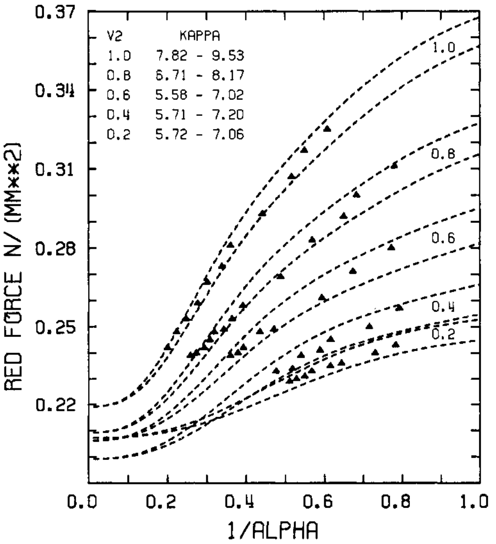

Figure 4. Reduced force as functions of α^{-1} for PBD swollen to varying degrees with 1,2,4-trichlorobenzene. The points represent experimental results of Mark et al.[6] for specimens of a sample cross-linked with sulfur and swollen to the extents indicated by the values of the volume fraction to the right of each isotherm and also in the inset in the upper left of this figure. The dashed curves were calculated according to theory with $\zeta = 0.0$ and κ values given in the inset.

within acceptable error limits.

The extent to which the ratio of high-elongation intercepts departs from unity is a measure of the error in the estimate of the cycle rank of a network arising from a Mooney–Rivlin treatment of stress–strain data. Although

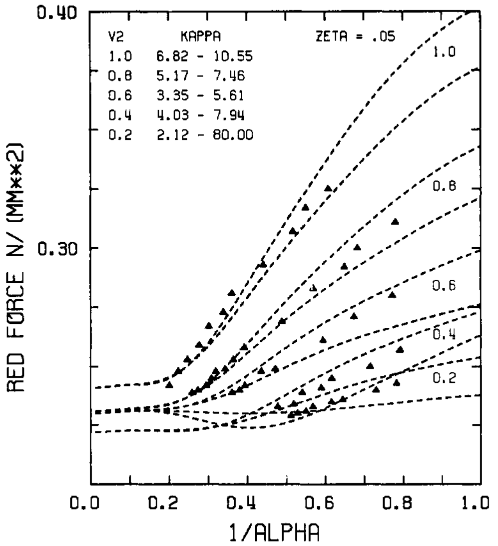

Figure 5. Same as Figure 4 but with $\zeta = 0.05$.

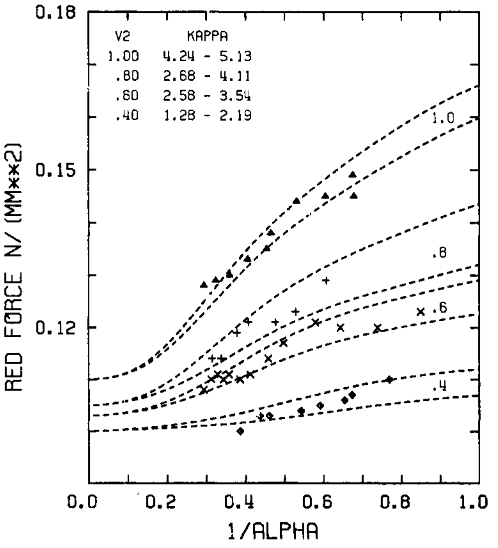

Figure 6. Reduced force as functions of α^{-1} for PIB swollen to varying degrees with 1,2,4-trichlorobenzene. The points represent experimental results of Rahalkar and Mark[9] for specimens swollen to the extents indicated by the values of the volume fraction to the right of each isotherm and also in the inset in the upper left of this figure. The dashed curves were calculated according to theory with $\zeta = 0.0$ and κ values given in the inset.

Table V
Values of the Reduced Stress at the Limits of High and Low Elongations

			high elongation			low elongation		
polymer	ϕ	v_2	$[f^*]_{ph}$, N mm^{-2}	$2C_1$,[a] N mm^{-2}	$2C_1/[f^*]_{ph}$	$[f^*]_{\alpha=1}$, N mm^{-2}	$2C_1 + 2C_2$,[a] N mm^{-2}	$(2C_1 + 2C_2)/[f^*]_{\alpha=1}$
PDMS*	4	1.00	0.0329	0.0304	0.924	0.0520	0.0571	1.10
		0.80	0.0311	0.0298	0.958	0.0450	0.0476	1.06
		0.60	0.0307	0.0299	0.0974	0.0410	0.0433	1.06
		0.40	0.0309	0.0305	0.987	0.0385	0.0398	1.03
PDMS	4	1.00	0.0246	0.0218	0.886	0.0430	0.0533	1.24
		0.80	0.0234	0.0220	0.940	0.0345	0.0365	1.06
		0.60	0.0222	0.0218	0.982	0.0315	0.0324	1.03
		0.40	0.0222	0.0208	0.937	0.0280	0.0290	1.04
PDMS	4	1.00	0.0143	0.0118	0.825	0.0255	0.0364	1.43
		0.80	0.0136	0.0121	0.890	0.0220	0.0255	1.16
		0.60	0.0133	0.0117	0.880	0.0195	0.0230	1.18
		0.40	0.0129	0.0126	0.977	0.0165	0.0168	1.02
PDMS	3	1.00	0.158	0.183	1.16		0.275	
	4	1.00	0.188	0.196	1.04		0.279	
	4.6	1.00	0.176	0.217	1.23		0.295	
	6	1.00	0.228	0.241	1.06		0.298	
	8	1.00	0.269	0.277	1.03		0.297	
	11	1.00	0.292	0.287	0.983		0.298	
	37	1.00	0.230	0.232	1.01		0.240	
PBD-S*	4	1.00	0.219	0.203	0.927	0.362	0.406	1.12
		0.80	0.209	0.202	0.967	0.321	0.343	1.07
		0.60	0.206	0.202	0.981	0.289	0.302	1.05
		0.40	0.199	0.196	0.985	0.261	0.272	1.04
		0.20	0.207	0.204	0.986	0.249	0.254	1.02
PBD-G	4	1.00	0.103	0.0904	0.878		0.280	
		0.80	0.100	0.0864	0.864		0.210	
		0.60	0.097	0.0915	0.943		0.167	
		0.40	0.093	0.0933	1.00		0.135	
		0.20	0.093	0.0878	0.944		0.117	
	24	1.00		0.0904			0.280	
		0.80	0.132	0.0868	0.658		0.210	
		0.60	0.127	0.0915	0.720		0.167	
		0.40		0.0933			0.135	
		0.20		0.0878			0.117	
PBD-P	4	1.00	0.150	0.142	0.947		0.228	
		0.80	0.144	0.140	0.972		0.178	
		0.60	0.142	0.138	0.972		0.160	
		0.40	0.136	0.138	0.01		0.150	
		0.20	0.142	0.135	0.951		0.144	
	24	1.00		0.142			0.228	
		0.80	0.149	0.140	0.940		0.178	
		0.60	0.145	0.138	0.952		0.160	
		0.40	0.142	0.138	0.972		0.150	
		0.20		0.135			0.144	
PIB	4	1.00	0.079	0.072	0.91	0.137	0.159	1.16
		0.80	0.079	0.083	1.05	0.106	0.103	0.972
		0.60	0.075	0.074	0.99	0.0925	0.0953	1.03
		0.40	0.071	0.073	1.03	0.0795	0.0777	0.977
PIB*	4	1.00	0.110	0.113	1.03	0.163	0.165	1.01
		0.80	0.105	0.0976	0.930	0.138	0.148	1.07
		0.60	0.103	0.104	1.01	0.126	0.131	1.03
		0.40	0.100	0.0905	0.905	0.110	0.115	1.04
PIB	4	1.00	0.130	0.128	0.985	0.187	0.194	1.04
		0.80	0.125	0.123	0.984	0.167	0.170	1.02
		0.60	0.118	0.114	0.966	0.140	0.145	1.04
		0.40	0.112	0.108	0.964	0.115	0.114	0.991
POE	3	1.000	0.691	0.744	1.08	0.934	0.934	1.00
		0.597	0.669	0.660	0.987	0.788	0.795	1.01
POE	3	0.565	0.589	0.613	1.04	0.722	0.722	1.00
		0.488	0.597	0.575	0.963	0.720	0.732	1.02
		0.390	0.605	0.593	0.980	0.710	0.715	1.01
POE*	3	0.429	0.250	0.251	1.00	0.316	0.320	1.01
		0.325	0.249	0.231	0.928	0.295	0.296	1,00
		0.220	0.244	0.263	1.08	0.274	0.266	0.971
POE	3	0.457	0.313	0.280	0.895	0.373	0.390	1.05
		0.341	0.330	0.329	0.997	0.388	0.402	1.04
		0.291	0.313	0.310	0.990	0.346	0.348	1.01
POP	3	1.00	1.25	1.24	0.992	1.37	1.37	1.00
POP	3	1.00	1.12	1.09	0.973	1.32	1.33	1.011
POP	3	1.00	0.538	0.628	1.17	0.932	0.929	0.997
POP	3	1.00	0.248	0.274	1.10	0.363	0.379	1.04
PTMO	3	1.00	0.691	0.747	1.08	1.01	1.01	1.00

Table V (Continued)

			high elongation			low elongation		
polymer	ϕ	v_2	$[f^*]_{ph}$, N mm^{-2}	$2C_1$,[a] N mm^{-2}	$2C_1/[f^*]_{ph}$	$[f^*]_{\alpha=1}$, N mm^{-2}	$2C_1 + 2C_2$,[a] N mm^{-2}	$(2C_1 + 2C_2)/[f^*]_{\alpha=1}$
PCL	3	1.000	2.52	2.47	0.980		3.70	
		0.775	2.52	2.87	1.14		3.48	
		0.558	2.52	2.98	1.18		3.47	
PCL	3	1.000	2.12	2.15	1.01		2.53	
		0.853	2.12	2.06	0.972		2.48	
		0.459	2.12	2.19	1.03		2.34	
PCL	3	1.000	1.15	1.40	1.22		2.18	
		0.766	1.18	1.39	1.18		1.99	
		0.394	1.23	1.33	1.08		1.99	
PCL	3	1.000	0.852	0.957	1.12		1.81	
		0.623	0.893	0.861	0.964		1.87	
		0.450	0.893	0.788	0.882		1.83	
		0.402	0.893	0.800	0.896		1.79	
PEA	4	1.00	0.075	0.081	1.08		0.115	
PEA	4	1.00	0.055	0.046	0.84		0.105	
PEA	4	1.00	0.043	0.036	0.84		0.0935	
PEA	4	1.00	0.044	0.037	0.84		0.0828	
PEA	4	1.00	0.031	0.018	0.58		0.0899	
PDMP	4	1.00	0.069	0.0527	0.76		0.118	
PPEP	4	1.00	0.013	0.00307	0.24	0.0213	0.0243	1.14

[a] Intercepts obtained from $[f^*] = 2C_1 + 2D_{2\alpha}{}^{-1}$.

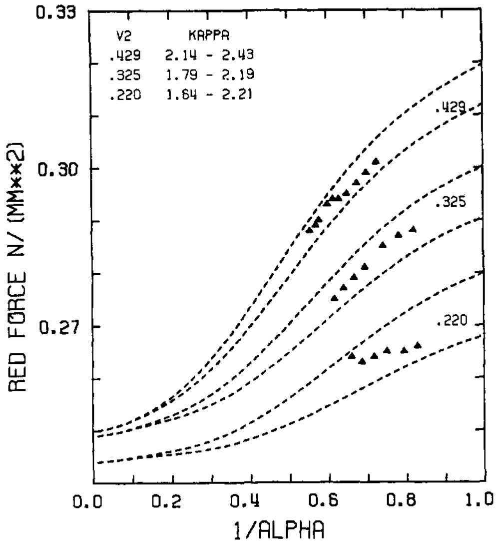

Figure 7. Reduced force as functions of α^{-1} for POE swollen to varying degrees with phenylacetate. The points represent experimental results of Mark and Sung[10] for specimens of a sample cross-linked with an aromatic triisocyanate and swollen to the extents indicated by the values of the volume fraction to the right of each isotherm and also in the inset in the upper left of this figure. The dashed curves were calculated according to theory with $\zeta = 0.0$ and κ values given in the inset.

this ratio is generally close to 1, there are both overestimates and underestimates, as expressed by ratios above and below 1, and in some instances significant departures from 1 are found.

Ratios of the low-elongation intercepts are uniformly close to 1, implying that little difference is observed between the results of the linear extrapolation and of a more detailed theoretical approach in the limit of $\alpha = 1$. Table V contains blanks for isotherms that were not theoretically investigated in the $\alpha = 1$ limit.

An examination of the $\zeta = 0$ curves reveals two details that are valid for every system studied as a function of dilution. First, a high-extension intercept, $[f^*]_{ph}$, can be found within ±5% of the mean $[f^*]_{ph}$ value for each network. It is found to be very nearly independent of the degree of swelling. Secondly, as the polymer volume fraction decreases, the κ values required to fit the experimental data also decrease. While reasonable values for the interpenetration parameter, J, for a given polymer can be determined, this parameter is not a universal constant but depends upon the nature of the polymer studied.

Conclusions

(1) A $[f^*]_{ph}$ value (±5%) proportional to the cycle rank of the network which is independent of polymer volume fraction is found to describe reduced-force data at $\alpha^{-1} = 0$.

(2) Increasing ζ above 0 does not improve the theoretical fit to reduced-force data.

(3) In general, as the polymer volume fraction decreases, the value of κ required to theoretically describe experimental data also decreases.

(4) An interpenetration parameter, J, can be determined for a given polymer; however, it is not a universal constant for every polymer.

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