Stress-Strain Isotherms for Stereoirregular and Stereoblock *Cis-Trans* Polybutadienes

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Gamma radiation and high-energy electrons were used to crosslink two types of polybutadiene (PBD), the first having random cis-trans-vinyl contents and the second consisting primarily of blocks of cis units and blocks of trans. The resulting elastomers were studied in elongation in the unswollen state, generally at 5°C, and in swelling equilibrium in a thermodynamically good solvent. Stress-strain isotherms obtained for the random-PBD networks did not show upturns in the reduced stress $[f^*]$ at high elongations, which is consistent with their non-crystallizability. The stereoblock polymers were found to be crystalline, with melting points ranging from 14 to 65°C. Attempts to achieve strain-induced crystallization in the stereoblock networks by judicious choice of temperature were unsuccessful as judged by the absence of any significant upturns in $[f^*]$. Values of the elasticity constants $2C_1$ and $2C_2$, and the molecular weight between crosslinks were similar to those obtained from the linear portions of the isotherms previously reported for high-cis and high-trans PBD, which readily undergo strain-induced crystallization.

INTRODUCTION

Polybutadiene (PBD) can be prepared so as to have 1,4 repeat units $[-CH_2-CH{=}CH-CH_2-]$ that are either cis or trans, or 1,2 vinyl units $[-CH_2-CH(CH{=}CH_2)-]$ of meso or racemic stereochemistry (1). Samples of PBD prepared using most catalysts or initiators have a random mixture of these units. They are highly elastomeric, but the irregularity of their structures is expected to greatly diminish their capacity for strain-induced crystallization (2–4), which is known to occur in high-cis (4–8) and high-trans PBD (8).

The elastomers of interest in the present investigation were prepared from samples of PBD which have neither high-cis nor high-trans contents. One type has random cis-trans-vinyl sequences, and the other is a stereoblock polymer having cis and trans sequence lengths ranging from 3 to 15. Stress-strain measurements in elongation are used to test for strain-induced crystallization (4, 9) and to obtain elasticity constants characterizing the structure of the networks (2, 10, 11). Swelling equilibrium measurements are also carried out to provide related information (2). Comparisons with the corresponding results obtained for high-cis and high-trans PBD (5–7) are used to elucidate the effects of regular stereochemical structure and the strain-induced crystallization which can result from it.

SOME EXPERIMENTAL DETAILS

Five samples of the random type of PBD were employed. Three were prepared by anionic polymerization and optionally by isomerization according to established methods (12) at Firestone specifically for this project, and two others were generously provided by Dr. S. L. Aggarwal of the General Tire and Rubber Company and Dr. G. Kraus of the Phillips Petroleum Company. Four stereoblock polymers were prepared (13) at the University of Liege. Microstructures determined for these various polymers by infrared spectroscopy (14) are given in columns two through four of *Table 1.* Melting points, determined by differential scanning calorimetry, and densities, determined by pycnometry (14), are given in the following two columns. Of the random polymers, only the one with 67.0 mol percent trans showed any evidence of crystallization, and then only at −20°C.

Crosslinking was accomplished by γ irradiations carried out at the University of Michigan, and electron-beam irradiations carried out at Firestone (8, 14). Details are given in columns seven and eight of the *Table.* Spectroscopic checks conducted after the irradiations showed that the microstructures were essentially unchanged, as was observed for high-cis and high-trans PBD (8, 14).

The networks were extracted as described elsewhere (8, 14), and then characterized with regard to their swelling in benzene at room temperature. The quantity of interest here is the volume fraction v_{2m} of polymer present in the network at swelling equilibrium (2).

The elongation isotherms were obtained on unswollen strips (~1.5 by 5.0 by 40. mm) cut from the extracted network sheets, with most of the data being obtained at 5°C. In the case of the stereoblock networks, the measurements were generally carried out at several temperatures, including the minimum temperature which would make the networks elastomeric. Some of the specific temperatures employed are given in column nine of *Table 1.*

The measurements were carried out in the usual manner (14-17), using an atmosphere of nitrogen to suppress oxidative degradation and rubber-lined clamps to minimize premature rupture. Most of the data were taken in the direction of increasing values of the elongation or relative length $\alpha = L/L_i$, but some were taken out of sequence to test for reversibility. Experiments were continued to the point of rupture (which generally occurred away from the clamps).

RESULTS AND DISCUSSION

The elongation results were interpreted in terms of the reduced stress or modulus (2, 4, 17, 18)

$$[f^*] \equiv f/[A^*(\alpha - \alpha^{-2})] \qquad (1)$$

where f is the equilibrium elastic force, and A^* is the undeformed cross-sectional area of the sample. Values of $[f^*]$ were plotted against reciprocal elongation α^{-1} as suggested by the equation (10, 17–19)

Table 1. Sample Characteristics, Cross-Linking Methods, and Elongation and Swelling Results

	Sample Characteristics					Crosslinking		Elongation Results					Swelling Results	
	Microstructure, Mol %													
Designation	Cis	Trans	Vinyl	Tm, °C	ρ,[b] g cm^{-3}	Radiation	Dose, Mrad.	T, °C	$2C_1$,[c] N mm^{-2}	$2C_2$,[c] N mm^{-2}	$2C_2/2C_1$	10^{-3} M_c,[d] g mol^{-1}	v_{2m}[e]	10^{-3} M_c,[d] g mol^{-1}
General Tire	25.0	67.0	8.0	−20.	0.979	γ	4.96	5.	0.044	0.166	3.76	25.8	0.0756	25.4
131-A					0.865		7.45		0.060	0.245	4.09	18.9	0.101	14.8
							9.93		0.106	0.226	2.13	10.7	0.132	8.74
							12.4		0.203	0.209	1.03	5.59	0.156	6.22
							14.9		0.242	0.297	1.22	4.69	0.168	5.33
							17.4		0.291	0.282	0.968	3.90	0.200	3.80
Firestone	31.6	66.7	1.6	None	0.900	e	14.2	5.	0.291	0.423	1.46	3.59	0.207	3.11
1515-73-3					0.789		19.0		0.359	0.375	1.04	2.91	0.241	2.22
							28.6		0.385	0.365	0.948	2.71	0.281	1.56
Firestone	34.0	55.0	11.0	None	0.885	γ	7.45	5.	0.053	0.315	5.98	19.4	0.119	9.59
Diene-35					0.772		9.93		0.137	0.296	2.12	7.50	0.160	5.27
							12.4		0.154	0.374	2.43	6.67	0.200	3.58
							14.9		0.217	0.333	1.54	4.73	0.197	3.39
							17.4		0.245	0.342	1.39	4.19	0.210	2.95
Firestone	35.0	63.1	1.9	None	0.900	e	14.3	5.	0.264	0.323	1.22	3.96	0.210	3.01
1515-79-2					0.789		19.3		0.325	0.346	1.07	3.21	0.239	2.26
							28.6		0.415	0.338	0.813	2.51	0.263	1.82
Phillips	43.0	47.0	10.0	None	0.943	γ	4.96	5.	0.034	0.212	6.22	32.2	0.0648	32.3
Solprene 255					0.822		7.45		0.052	0.342	6.58	21.0	0.0805	21.4
							9.93		0.101	0.398	3.93	10.8	0.134	8.05
							12.4		0.215	0.267	1.24	5.09	0.155	5.99
							14.9		0.231	0.291	1.26	4.73	0.169	5.00
							17.4		0.250	0.371	1.45	4.37	0.183	4.22
Stereoblock 3[a]	49.0	42.0	9.0	65.	~0.9	γ	11.9	25.	0.211	0.089	0.422	10.7	0.144	7.64
A–D 5	53.0	44.0	3.0	14.	~0.9		11.9	5.	0.136	0.276	2.03	15.5	0.158	6.31
6	37.0	58.0	5.0	21.	~0.9		11.9	65.	0.104	0.192	1.48	24.4	0.129	9.54
15	47.0	49.0	4.0	46.	~0.9		11.9	66.	0.197	0.412	2.10	13.0	0.156	6.48

[a] Number of units per stereosequence.
[b] Density at 5 and 25°C, respectively.
[c] Elasticity constants in the equation $[f^*] = 2C_1 + 2C_2\alpha^{-1}$ for the reduced stress.
[d] Molecular weight between crosslinks.
[e] Volume fraction of polymer at equilibrium swelling in benzene at room temperature.

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

where $2C_1$ and $2C_2$ are constants independent of α.

The isotherms for the stereochemically random PBD networks are shown in *Figs. 1* to *4*. The reversibility is generally satisfactory and the results are well represented by the least-square lines shown. There are no upturns in the reduced stress, which is consistent with the non-crystallizability of these polymers. In the case of the high-trans polymers studied previously (8, 14), large amounts of crystallinity were observed for trans contents as low as 72 mol percent, but these polymers were relatively blocky.

The four stereoblock polymers were found to be crystalline, with melting points as cited in *Table 1*. Stress-strain isotherms were determined at several temperatures, and some of the results are shown in *Fig. 5*. The tabulated results pertain to temperatures just high enough to make the networks elastomeric. At none of the temperatures employed was it possible to induce significant amounts of additional crystallinity, as would have been evidenced by upturns in the reduced stress. The amount of crystallinity must therefore have been relatively insensitive to deformation over the temperature and elongation ranges investigated.

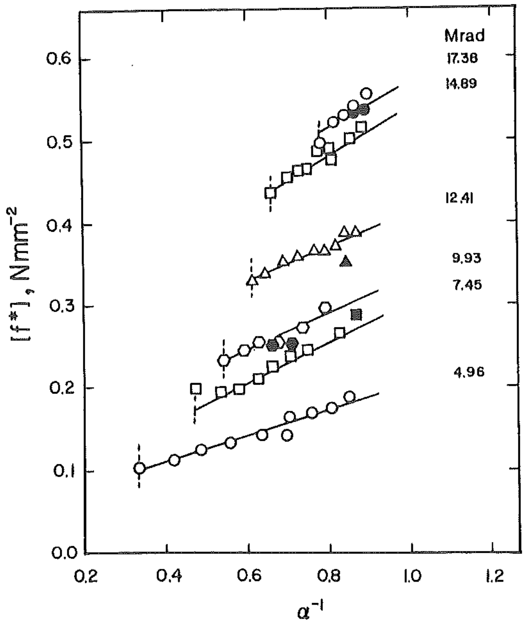

Fig. 1. Stress-strain isotherms at 5°C for the (stereochemically random) 131-A PBD networks cured by γ-radiation. Each of these isotherms is labelled with the radiation dose the sample received, and the rupture points are shown by dashed vertical lines. Results were generally obtained using a series of increasing values of the elongation α. Results obtained out of sequence to check for reversibility are shown by the filled symbols.

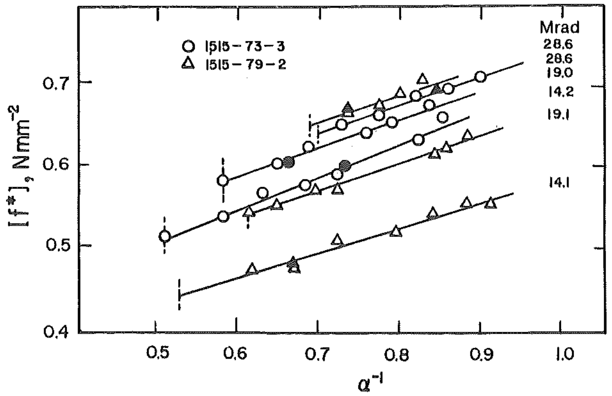

Fig. 2. Stress-strain isotherms at 5°C for the 1515-73-3 and 1515-79-2 networks.

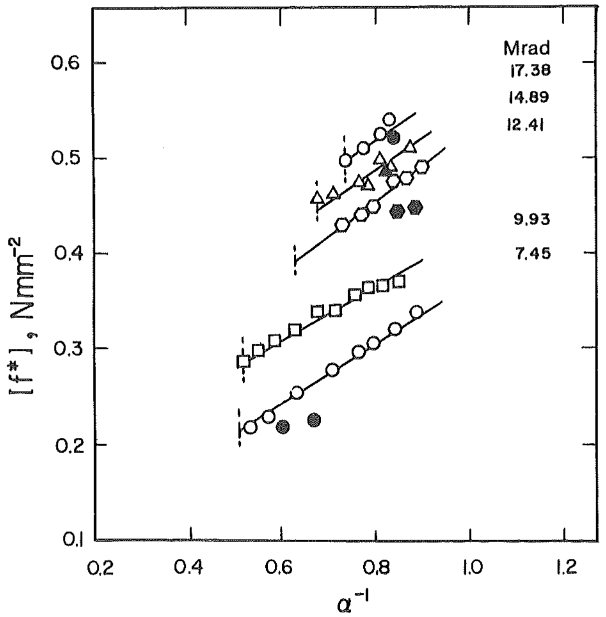

Fig. 3. Stress-strain isotherms at 5°C for the Diene-35 networks.

Values of the elongation constants $2C_1$, $2C_2$, and $2C_2/2C_1$ obtained from least-squares analysis of the isotherms are given in columns ten through twelve in *Table 1*. The constant $2C_1$ is a direct measure of the crosslink density or inverse measure of the molecular weight M_c between crosslinks (19). It was found to increase with increase in radiation dose, as expected. The other constants, $2C_2$ and $2C_2/2C_1$, are due to increase in nonaffineness of the deformation with increase in elongation (20). The values are generally large, which suggests a heterogeneous distribution of crosslinks of relatively high functionality (21). In any case, decrease in M_c should decrease the amount of chain-junction entangling which, in turn, should decrease the extent to which the network deformation can become more nonaffine with increasing elongation (11, 20). The relevant results for the five types of random networks are shown in *Fig. 6*. Two curves are seen to represent all of the results and both show the expected (20) decrease of $2C_2/2C_1$ toward zero as M_c decreases.

Values of M_c were calculated from the relationship (11, 17, 20)

$$M_c \simeq A_\phi \rho RT/2C_1 \qquad (3)$$

where ρ is the network density, R is the gas constant, and T is the absolute temperature. The structure factor A_ϕ is given by (11, 20)

$$A_\phi = 1 - 2/\phi \qquad (4)$$

where ϕ is the junction functionality; it should therefore be ½ for the usual functionality of four. Values of M_c thus calculated are given in column thirteen of *Table 1*. They are, of course, only approximate because of difficulties in the extrapolations for the $2C_1$ estimate of the high deformation modulus (22) and uncertainty in the most appropriate value to use for A_ϕ.

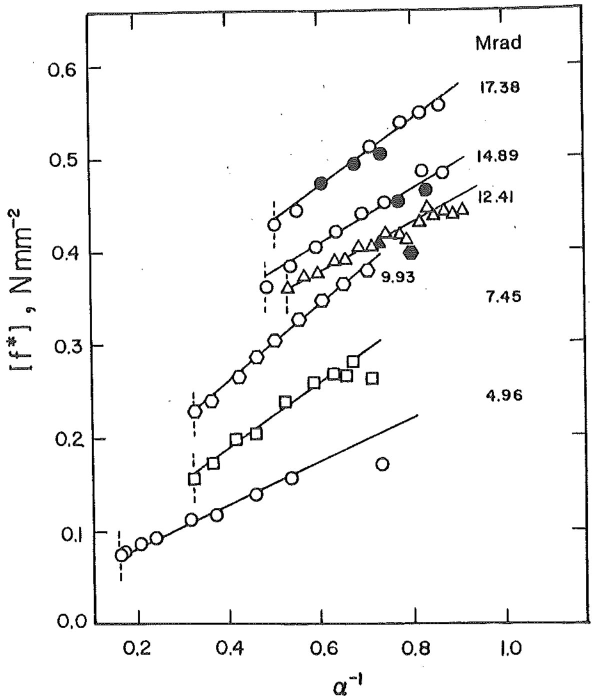

Fig. 4. Stress-strain isotherms at 5°C for the Phillips Solprene 255 networks.

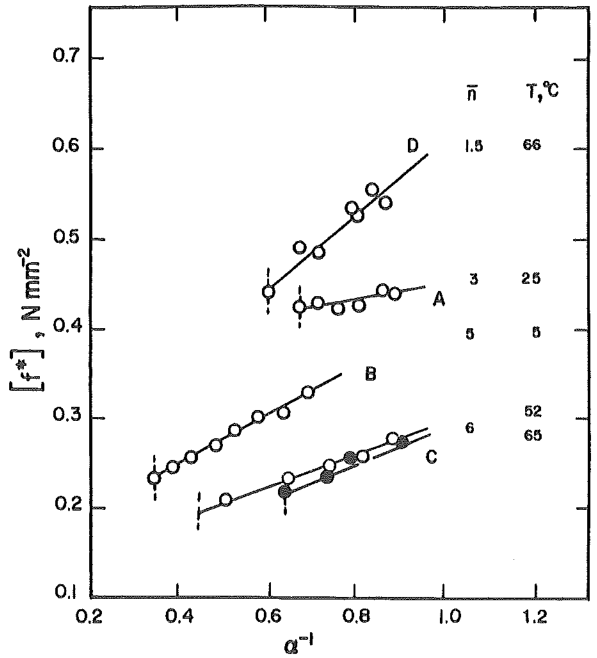

Fig. 5. Typical stress-strain isotherms for the stereoblock networks. Each isotherm is labelled with the network designation, and the temperature at which it was determined. The isotherm for n = 3 has been shifted upward by 0.15 N mm⁻² in order to prevent overlapping of some of the points.

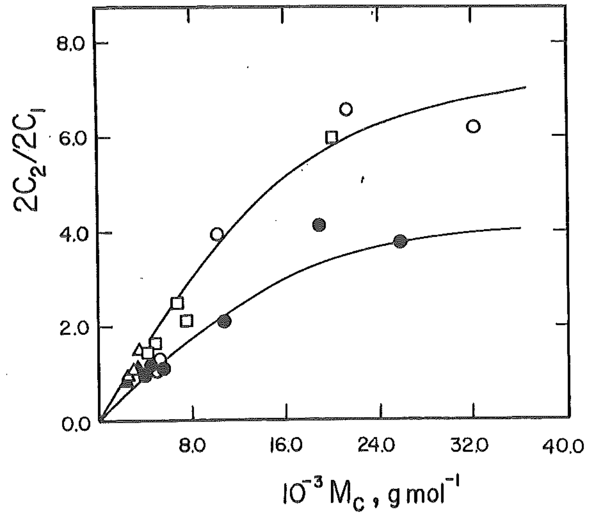

Fig. 6. The elasticity constant $2C_2$ normalized to constant cross-link density (as specified by $2C_1$) shown as a function of the average molecular weight between crosslinks. The results pertain to networks 131-A (●), 1515-73-3 (△), Diene-35 (□), 1515-79-2 (▲), and Phillips Solprene 255 (○).

Alternative values of M_c were obtained from the swelling results through the relationship (2, 5, 10, 22)

$$M_c = -\rho V_1(v_{2m}^{1/3} - v_{2m}/2)/[\ln(1 - v_{2m}) + v_{2m} + X_1 v_{2m}^2] \qquad (5)$$

where V_1 is the molar volume of the benzene and X_1 is the free energy of interaction parameter (2) for polybutadiene in benzene. Reliable values of X_1 as a function of composition are not available, unfortunately, and the constant value 0.325 (5) reported for a polybutadiene sample of unspecified stereochemical composition (23) had to be used. The experimental values of v_{2m} and the values of M_c they yield are given in the final two columns of *Table 1*. These estimates of M_c are seen to be in very good agreement with those obtained from the elongation results. The agreement is much better than was obtained in the case of the crystallizable PBD elastomers (8, 14). In that case, there were probably difficulties in the extrapolations for $2C_1$ arising from the strain-induced crystallization, and there may have been more of a difference between the stereochemical compositions of these samples and the PBD sample used to obtain the cited value of X_1 (23).

The present results clearly demonstrate the effects of stereochemical structure on several elastomeric properties. A detailed analysis (14) of its effect specifically on ultimate properties will be reported elsewhere (24).

ACKNOWLEDGMENTS

JEM wishes to acknowledge with gratitude the financial support provided by the National Science Foundation through Grant DMR-7918903 (Polymers Program, Division of Materials Research), and the hospitality of the IBM Research Laboratory, San Jose, during a sabbatical visit when the manuscript was written. We also wish to thank Mr. T. Ryle for carrying out the differential scanning calorimetry measurements, and the Phoenix Laboratory at the University of Michigan for assistance in the γ irradiations.

REFERENCES

1. G. Odian, "Principles of Polymerization," 2nd Ed., Wiley-Interscience, New York, NY (1981).
2. P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, NY (1953).
3. L. Mandelkern, "Crystallization of Polymers," McGraw-Hill, New York, NY (1964).
4. J. E. Mark, *Polym. Eng. Sci.*, **19**, 409 (1979).
5. T.-K. Su and J. E. Mark, *Macromolecules*, **10**, 120 (1977).
6. D. S. Chiu, T.-K. Su, and J. E. Mark, *Macromolecules*, **10**, 1110 (1977).
7. A. De Chirico, P. C. Lanzani, E. Raggi, and M. Bruzzone, *Makromol. Chemie*, **175**, 2029 (1974).
8. M. A. Sharaf, J. E. Mark, and S. Cesca, ms. submitted to *Polym. Eng. Sci.*
9. J. E. Mark, *Polym. Eng. Sci.*, **19**, 254 (1979).
10. L. R. G. Treloar, "The Physics of Rubber Elasticity," 3rd Ed., Clarendon Press, Oxford (1975).
11. J. E. Mark, *Adv. Polym. Sci.*, **44**, 1 (1982).
12. D. N. Schulz, S. R. Turner, and M. A. Golub, *Rubber Chem. Technol.*, **55**, 809 (1982).
13. Ph. Teyssié, A. Devaux, P. Hadjiandreou, M. Julémont, J. M. Thomassin, E. Walckiers, and R. Warin in "Preparation and Properties of Stereoregular Polymers", Vol. 51, Ed. by R. W. Lenz and F. Ciardelli, D. Reidel Pub. Co., Dordrecht, The Netherlands (1980); also, manuscripts in preparation.
14. M. A. Sharaf, Ph.D. thesis in Chemistry, The University of Michigan (1979).
15. J. E. Mark, *J. Am. Chem. Soc.*, **92**, 7252 (1970).
16. R. M. Johnson and J. E. Mark, *Macromolecules*, **5**, 41 (1972).
17. J. E. Mark and J. L. Sullivan, *J. Chem. Phys.*, **66**, 1006 (1977).
18. J. E. Mark and P. J. Flory, *J. Appl. Phys.*, **37**, 4635 (1966).
19. J. E. Mark, *Rubber Chem. Technol.*, **48**, 495 (1975).
20. P. J. Flory, *Proc. R. Soc. London A*, **351**, 351 (1976).
21. R. W. Brotzman and P. J. Flory, ms. submitted to *Macromolecules*.
22. J. E. Mark, *Rubber Chem. Technol.*, **55**, 762 (1982).
23. R. S. Jessup, *J. Res. Nat. Bur. Stand.*, **60**, 47 (1958).
24. M. A. Sharaf, ms. in preparation.

Ethylamine and Ammonia as Catalysts in the In-Situ Precipitation of Silica in Silicone Networks*

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Both ethylamine and ammonia in aqueous solutions catalyze the hydrolysis of tetraethylorthosilicate to precipitate silica filler within poly(dimethylsiloxane) elastomers. The rate of filler precipitation can vary in a complex manner, possibly due to loss of colloidal silica and, in the case of the ethylamine solutions, deswelling of the networks. Increase in catalyst concentration increases the precipitation rate, and increase in amount of filler precipitated dramatically increases the modulus and ultimate strength of the networks, thus demonstrating the desired reinforcing effects.

INTRODUCTION

Silica filler may be precipitated into an already cross-linked elastomer by the hydrolysis

$$Si(OC_2H_5)_4 + 2H_2O \rightarrow SiO_2 + 4C_2H_5OH \quad (1)$$

of tetraethylorthosilicate (TEOS) present as diluent in the network structure (1–6). The concept of such an "in-situ" precipitation is novel, and of practical importance since hard mineral fillers, however introduced, can give considerable reinforcement to an elastomer (7–11). A variety of substances have been found (2) to act as catalyst for this hydrolysis, but very little has been done to characterize the rate of the reaction.

The present study concerns the use of aqueous solutions of ethylamine and ammonia as catalysts for this in-situ precipitation reaction. They were chosen in part because of their volatility, which makes them easy to remove from the filled polymer network. Of primary interest is the effect of the hydrolysis conditions on the amount of silica precipitated and the elastomeric properties of the resulting filled elastomers.

EXPERIMENTAL DETAILS

The networks investigated were prepared from two samples of hydroxyl-terminated poly(dimethylsiloxane) (PDMS) [—$Si(CH_3)_2O$—] having number-average molecular weights of 8.0 and 21.3 × 10^3 g mol^{-1}, respectively. The samples were generously provided by the Dow Corning Corporation of Midland, MI. They were tetrafunctionally end linked using $Si(OC_2H_5)_4$ with stannous-2-ethylhexanoate as catalyst, in the usual manner (12, 13). The resulting networks were extracted with tetrahydrofuran and then toluene for several days to remove soluble material (found to be present to the extent of a few percent).

Two series of samples were cut from the extracted and dried network sheets. The first consisted of a large number of relatively small pieces to be used to obtain the amount of filler precipitated as a function of hydrolysis time. The second consisted of a smaller number of larger pieces, in the form of strips suitable for stress-strain measurements in elongation. (The dependence of the wt percent filler on time and catalyst concentration can be expected to differ somewhat for the two series since the TEOS hydrolysis and its loss to the surrounding solution would depend on the ratio of sample surface area to volume, and thus on sample size and shape).

One strip cut from each network sheet was set aside as a reference material (0 wt percent filler). The other network strips were swelled with TEOS to the maximum extent attainable, which corresponded to a volume fraction of polymer of approximately 0.3 and 0.2, respectively. The swollen strips were then placed into aqueous solutions of either ethylamine or ammonia, at a series of concentrations. The hydrolysis of the TEOS was permitted to occur at room temperature for various periods of time, and values of the wt percent filler incorporated, were obtained from the weights of the dried strips.

The strips cut from the networks were used in elongation experiments to obtain the stress-strain isotherms at 25°C (12–15). The elastomeric properties of primary interest were the nominal stress $f^* \equiv f/A^*$ (where f is the equilibrium elastic force and A^* the undeformed cross-sectional area), and the reduced stress or modulus (15–18) $[f^*] \equiv f^*/(\alpha - \alpha^{-2})$ (where $\alpha = L/L_i$ is the elongation or relative

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*Presented in part at a meeting of the Rubber Division of the American Chemical Society, Los Angeles, 1985.