Supplementary Material Available: Experimental diffusion coefficients of Na^+, Ca^{2+}, and SO_4^{2-} (Tables I and II) (2 pages). Ordering information is given on any current masthead page.

References and Notes

(1) H. Noguchi and A. Rembaum, *Macromolecules*, **5**, 253, 261 (1972).
(2) H. Noguchi and A. Rembaum, *J. Polym. Sci., Polym. Lett. Ed.*, **7**, 383 (1969).
(3) M. Kowblansky and P. Ander, *J. Phys. Chem.*, **80**, 297 (1976).
(4) A. Kowblansky, R. Sasso, V. Spagnuola, and P. Ander, *Macromolecules*, **10**, 78 (1978).
(5) P. Ander, G. Gangi, and A. Kowblansky, *Macromolecules*, **11**, 904 (1978).
(6) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions", Butterworths, London, 1959.
(7) J. C. Anderson and K. Saddington, *J. Chem. Soc.*, 5381 (1949).
(8) See paragraph at end of text regarding supplementary material.
(9) P. Turq, Ph.D. Thesis, University of Paris, Paris, France, 1970.
(10) S. Menezes-Affonso and P. Ander, *J. Phys. Chem.*, **78**, 1756 (1974).
(11) M. Kowblansky, M. Tomasula, and P. Ander, *J. Phys. Chem.*, **82**, 1491 (1978).
(12) H. Magdelenat, P. Turq, M. Chemla, and B. Para, *Biopolymers*, **15**, 175 (1976).
(13) H. Magdelenat, P. Turq, M. Chemla, and B. Para, *Biopolymers*, **13**, 1535 (1974).
(14) G. S. Manning, *J. Chem. Phys.*, **51**, 924, 934 (1969).
(15) G. S. Manning, "Polyelectrolytes", E. Selegny, Ed., D. Reidel Publishing Co., Dordrecht, Holland, 1974.
(16) G. S. Manning, *Biophys. Chem.*, **7**, 95 (1977).
(17) G. S. Manning, *Q. Rev. Biophys.*, **11**, 179 (1978).

Effect of Chain Length Distribution on Elastomeric Properties. 2. Comparisons among Networks of Varying Degrees of Randomness[1]

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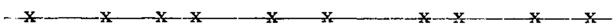
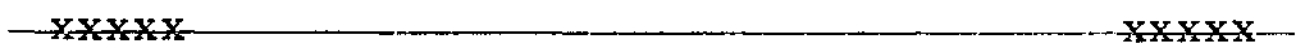
ABSTRACT: Three poly(dimethylsiloxane) polymers were prepared, all with 0.5 mol % methylvinylsiloxane units. In the first polymer the potentially reactive vinyl groups were randomly distributed, in the second they were segregated in groups but slightly separated from one another, while in the third the vinyl groups were strictly segregated and adjacent. Networks were prepared from each of the polymers and from mixtures thereof. They were characterized in terms of their stress–strain isotherms in elongation and their degree of equilibrium swelling. Previous observation showed that networks prepared by selectively cross-linking through segregated vinyl sites resulted in relatively large values of the molecular weight M_c between cross-links. The present study showed that the cross-linking agent 2,5-dimethyl-2,5-bis(*tert*-butylperoxy)hexane is considerably more selective toward vinyl groups than is benzoyl peroxide, in that it does yield networks which reflect the segregated vinyl distribution. Relatively large values of M_c persist even when the vinyl groups are somewhat separated, thus implicating the elastic ineffectiveness of very short network chains (rather than a reduced reactivity of cross-linking sites when situated on every Si atom in a portion of the chain). The ratio $M_c(f)/M_c(v_{2m})$ of the values of M_c from stress–strain and swelling measurements was also found to depend on the nonrandomness of the cross-link distribution.

In two previous studies,[3,4] elastomeric networks were prepared from two samples of poly(dimethylsiloxane) (PDMS), both with 0.57 mol % methylvinylsiloxane units. In the first polymer, the potentially reactive vinyl groups were randomly distributed



while in the second they were completely segregated, in adjacent repeat units,



at the two end of the chains. The networks were prepared from both polymers and from various mixtures thereof, using γ radiation and benzoyl peroxide (which are not selective for vinyl groups) and a silicon hydride cross-linking agent $Si[OSi(CH_3)_2H]_4$ (which is very highly selective).[5-7] They were characterized in terms of their stress–strain isotherms in elongation and their degree of equilibrium swelling in benzene.[4] The networks which had been prepared by selectively cross-linking through the segregated vinyl sites were found to have relatively large values of the molecular weight M_c between cross-links, thus indicating that very short chains have significantly reduced contributions to the elastomeric properties of a network. The ratio $M_c(f)/M_c(v_{2m})$ of the values of M_c from the stress–strain isotherm and degree of equilibrium swelling was generally found to be close to the expected value of unity. The values of the ratio for the very nonrandom networks suggested, however, that the very short chains contributed even less to the swelling response than they did to the modulus in elongation.[4]

The present study addresses two related aspects of this general problem of characterizing the effect of chain length distribution on elastomeric properties and serves in a sense to check the conclusions reached in the previous studies.[3,4] The first aspect involves the use of 2,5-dimethyl-2,5-bis(*tert*-butylperoxy)hexane $[CH_3C(CH_3)(OOC_4H_9)CH_2-]_2$ (DBPH) as a cross-linking agent for the same two PDMS polymers. Free radicals generated from it are much less reactive than those generated from benzoyl peroxide and, as a result, do have a significant selectivity for vinyl groups.[6,7] Networks thus prepared should therefore have properties similar to those of the networks prepared by the previously employed highly selective cross-linking

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Table I
Polymer Structure, Composition of the Polymer Mixtures, and Elastomeric Properties of the Resulting Networks

		elongation[a]			swelling[c]		
vinyl spacing[e]	F_s[f]	$2C_1$, N mm^{-2}	$2C_2$, N mm^{-2}	$10^{-3}M_c(f)$,[b] g mol^{-1}	v_{2m}	$10^{-3}M_c(v_{2m})$,[b] g mol^{-1}	$M_c(f)/M_c(v_{2m})$
adjacent units	0.00	0.1505	0.1148	7.98	0.283	8.33	0.958
	0.25	0.1406	0.0947	8.55	0.265	10.2	0.838
	0.75	0.0854	0.0965	14.1	0.223	16.7	0.844
	1.00	0.0516	0.0759	23.3	0.186	26.9	0.866
every 6th unit	0.00	0.1505	0.1148	7.98	0.283	8.33	0.958
	0.25	0.1241	0.0812	9.68	0.252	11.8	0.820
	0.75	0.0591	0.0659	20.0	0.193	24.4	0.820
	1.00	0.0286	0.0348	42.0	0.130	61.8	0.680

[a] In the unswollen state, at 25 °C. [b] Molecular weight between cross-links. [c] In benzene, at 25 °C. [d] Volume fraction of polymer in the network at swelling equilibrium. [e] Vinyl spacing in chains with segregated sites. [f] Fraction of chains with segregated sites.

technique.[4] The second aspect involves the use of a specially prepared PDMS polymer in which the vinyl groups are still segregated at the chain ends but are spaced at approximately every sixth unit instead of at adjacent units.

—x—x—x—x—x———————————x—x—x—x—x—

Cross-linkages formed at these sites should again yield network chains too short to be elastically effective, but the increased spacing would facilitate the cross-linking reaction if it had been hindered by proximity effects in the case of the chains with adjacent vinyl groups.

Experimental Section

All of the PDMS polymers used in the study contained approximately 0.57 mol % methylvinylsiloxane units, as determined by titration[8] with iodine monochloride, and had relatively high number-average molecular weights (0.15–0.30×10^6 g mol^{-1}). The random polymer was prepared by copolymerizing a mixture of dimethyl and methylvinyl cyclic siloxanes, using potassium silanolate as equilibrating catalyst to further disperse the vinyl groups along the chain.[9] The polymer with the segregated and adjacent vinyl groups, synthesized and generously provided by A. Ward of the Dow Corning Corporation, was polymerized from cyclic siloxane trimer, using dianionic "living polymer" techniques[10] to assure that the methylvinylsiloxane units were all located adjacently in blocks at the two ends of the chain. The polymer with the segregated but separated vinyl groups was prepared in a two-step procedure.[11] First, the blocks containing the relatively high vinyl concentration were prepared by reacting Me_2SiCl_2, cyclic $[Si(CH_3)(CH{=}CH_2)O-]_x$, and cyclic $[Si(CH_3)_2O-]_x$ with fuming sulfuric acid, added dropwise. After the mixture had reacted for 2 h at 30 °C and for 20 h at 50 °C, chlorine-terminated blocks with 15 mol % $[Si(CH_3)(CH{=}CH_2)O-]$ randomly distributed along the chains resulted. These blocks were then reacted with hydroxyl-terminated blocks of $[Si(CH_3)_2O-]_x$ in a mixture of pyridine and toluene at room temperature. The resulting polymer was neutralized with NH_4OH, washed with water, and then washed with 2-propanol. Volatiles were removed by heating under vacuum. Two intermediate degrees of block-like structure or segregation of vinyl units were obtained by mixing various amounts of the two vinyl-segregated polymers with the random copolymer. The chosen values of the fraction F_s of chains in the mixture having the vinyl cross-linking sites located at the ends were 0.25 and 0.75, as well as the limiting values of 0.00 and 1.00.

The cross-linking technique employed was very similar to that previously used in the benzoyl peroxide cures[4] and involved maintaining the DBPH–PDMS systems at 170 °C for 1 h. In the case of the mixtures involving the PDMS chains with the adjacent vinyl groups, two series of networks were prepared, at DBPH concentrations of 0.5 and 0.4 wt %, respectively. For the mixtures involving the chains with the slightly separated vinyl groups, 0.5 wt % of the DBPH was employed.

The networks thus prepared were extracted with benzene and dried. They were then studied in elongation and in equilibrium swelling in benzene, both at 25 °C, exactly as was described previously.[4]

Results and Discussion

The equilibrium values of the reduced stress $[f^*]$[12-14] obtained from the elongation measurements were plotted against reciprocal elongation, as suggested by the semiempirical equation of Mooney and Rivlin[15] in which $2C_1$

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

and $2C_2$ are constants independent of α. The isotherms thus obtained were very similar to those obtained in the earlier studies[3,4] with regard to the range of elongation covered and the degree of reproducibility. The values of the constants $2C_1$ and $2C_2$ characterizing each isotherm were obtained by least-squares analysis. The results are given in columns three and four of Table I for the two series of networks prepared by using 0.5 wt % DBPH. The constant $2C_2$ increases with an increase in $2C_1$, as is usually the case for this range of M_c,[13] but there does not seem to be any significant difference in the values of the ratio $2C_2/2C_1$ for the two series of networks. According to the most recent theories of rubberlike elasticity,[15,18] this ratio is a measure of the extent to which the elastic deformation changes from affine to nonaffine with increasing stress and is thus related to the looseness with which the cross-links are embedded within the network structure. Simply averaging the values in the two series yields $2C_2/2C_1 = 1.01$ (± 0.29) and 0.94 (± 0.23), respectively, in good agreement with the theoretically predicted value of approximately unity for a tetrafunctional network.[16,17]

The values of $2C_1$ were used to calculate stress–strain values $M_c(f)$ of the molecular weight between cross-links by means of the equation[16,17,21]

$$M_c(f) = A_4\rho kT/2C_1 \qquad (2)$$

in which $A_4 = {}^1/_2$,[16,17] ρ is the density of the network, and kT is the product of the Boltzmann constant and the absolute temperature, 298.2 K. The most pertinent values of $M_c(f)$ are shown as a function of the degree F_s of vinyl site segregation in Figure 1. The networks prepared by using benzoyl peroxide[4] show only a slight increase in $M_c(f)$ with F_s; essentially the same behavior was shown by those prepared by using γ radiation.[4] The networks prepared by using the $Si[OSi(CH_3)_2H]_4$ reaction, however, show a very much larger increase.[4] Most significantly, the networks prepared by using the DBPH also showed a significant increase in $M_c(f)$.[19] These results are readily interpreted by noting that $M_c(f)$ is directly proportional to the structure factor but inversely proportional to the number of elastically effective chains, i.e., $M_c(f) \propto (1 - 2/\phi)N^{-1}$. If the spacing between two cross-links becomes too small, the intervening chain must become elastically rather ineffective, and the two cross-links act approxi-

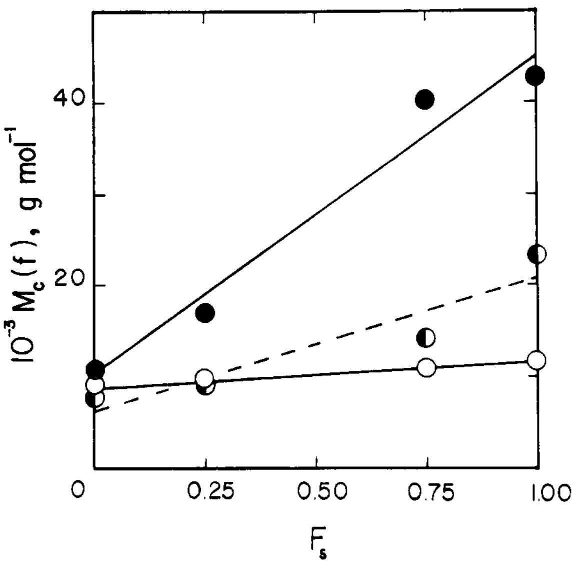

Figure 1. Values of the molecular weight M_c between cross-links, as calculated from the stress-strain isotherms, for some of the networks prepared from the PDMS chains with adjacent vinyl groups. The results are shown as a function of the fraction of chains having the cross-linking sites segregated at the ends of the chains. The three types of networks were prepared by benzoyl peroxide (○),[4] $Si[OSi(CH_3)_2H]_4$ (●),[4] and DBPH (◐).

mately as a single cross-link of higher functionality.[4] As is evident from the form of the product $(1 - 2/\phi)N^{-1}$, the increase in functionality ϕ is not sufficient to offset the decrease in N, and $M_c(f)$ increases correspondingly. Thus, the results confirm the expectation that the DBPH cross-linking agent does have a selectivity for vinyl groups and support the previous conclusions[4] regarding the possible effects of chain length distribution on elastomeric properties.

As is shown in the lower portion of the table, this effect of cross-link segregation on $M_c(f)$ is in strong evidence even when the segregated cross-linking sites are spaced approximately six units apart. This suggests that the vinyl to $Si[OSi(CH_3)_2H]_4$ cross-linking reaction is not very significantly affected by vinyl-vinyl proximity effects.

The values of the volume fraction v_{2m} of polymer in each of the networks at swelling equilibrium in benzene at 25 °C are given in column six of the table. They were interpreted in terms of the classic equation[20-22]

$$M_c(v_{2m}) = -A_4 \rho V_1 v_{2m}^{1/3} / [\ln (1 - v_{2m}) + v_{2m} + \chi_1 v_{2m}^2] \tag{3}$$

in which V_1 is the molar volume of the benzene and χ_1 is the free energy of interaction parameter[14,20] between the benzene and the PDMS networks. The resulting values of $M_c(v_{2m})$ and $M_c(f)/M_c(v_{2m})$ are given in the last two columns of the table.[23] These results suggest a possible decrease in this ratio with increasing cross-link segregation similar to that observed in the case of the very selective $Si[OSi(CH_3)_2H]_4$ system.[4] Although this further suggests that the very short chains may contribute even less to the swelling response than they do to the modulus in elongation, more experimental data will obviously be required to provide a definitive answer to this problem.

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References and Notes

(1) Presented in preliminary form before the Rubber Division of the American Chemical Society, Boston, 1978.
(2) Dow Corning Corporation, Midland, Mich. 48640.
(3) J. R. Falender, G. S. Y. Yeh, and J. E. Mark, *J. Chem. Phys.*, **70**, 5324 (1979).
(4) Paper 1: J. R. Falender, G. S. Y. Yeh, and J. E. Mark, *J. Am. Chem. Soc.*, in press.
(5) A. Chapiro, "Radiation Chemistry of Polymeric Systems", Wiley-Interscience, New York, 1962.
(6) M. L. Dunham, D. L. Bailey, and R. Y. Mixer, *Ind. Eng. Chem.*, **49**, 1373 (1957).
(7) P. G. Bork and C. W. Roush in "Vulcanization of Elastomers", G. Alliger and I. J. Sjothun, Eds., Rheinhold, New York, 1964.
(8) R. C. Smith, N. C. Angelotti, and C. L. Hanson in "Analysis of Silicones", A. L. Smith, Ed., Wiley-Interscience, New York, 1974.
(9) W. T. Grubb and R. C. Osthoff, *J. Am. Chem. Soc.*, **77**, 1405 (1955).
(10) J. C. Saam and F. W. G. Fearon, U.S. Patent 3678125 (1972).
(11) K. Itoh, N. Kuga, and T. Fukuda (Shin-Etsu Chemical Co., Ltd), U.S. Patent 3950299 (1976).
(12) J. E. Mark and P. J. Flory, *J. Appl. Phys.*, **37**, 4635 (1966).
(13) J. E. Mark, *Rubber Chem. Technol.*, **48**, 495 (1975).
(14) P. F. Flory and Y. Tatara, *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 683 (1975).
(15) G. Ronca and G. Allegra, *J. Chem. Phys.*, **63**, 4990 (1975).
(16) P. J. Flory, *Proc. R. Soc. London, Ser. A*, **351**, 351 (1976).
(17) P. J. Flory, *J. Chem. Phys.*, **66**, 5720 (1977).
(18) P. J. Flory, *Macromolecules*, **12**, 119 (1979).
(19) The networks formed by using the lower weight percent of DBPH were very lightly cross-linked and therefore very difficult to characterize. They did give results, however, in agreement with the more reliable results shown in Table I.
(20) P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, N.Y., 1953.
(21) J. E. Mark and J. L. Sullivan, *J. Chem. Phys.*, **66**, 1006 (1977).
(22) J. E. Mark, *J. Am. Chem. Soc.*, **92**, 7252 (1970).
(23) The preliminary results reported previously [Paper No. 4, Meeting of Rubber Division, ACS, Boston, 1978] were calculated by using swelling equation parameters now thought to be less appropriate than those used in the present analysis.