$(k_{p12}''/k_{p12}' < k_{p22}''/k_{p22}')$.[22] Furthermore this is also the case as attacking monomers become more reactive $(k_{p12}''/k_{p12}' < k_{p11}''/k_{p11}')$.

In summary, we state that the rate of the copolymerization can be increased by the field and the increase is due to the field-facilitated dissociation of growing chain ends. Furthermore, the monomer reactivity ratios can be changed; the less reactive monomer can be more easily incorporated into the copolymers in the presence of the field than in its absence. This finding is also explainable in terms of the shift of the dissociation state by the field.

(22) It cannot presently be concluded whether this interpretation is of a wide validity. Some data available now on living anionic polymerizations do not agree with this interpretation. However, the values of the rate constants reported for the living systems vary from author to author, evidently on the basis of the experimental difficulty.

The Diffusion of Radioactively Tagged *n*-Hexadecane and *n*-Dodecane through Rubbery Polymers. Effects of Temperature, Cross-Linking, and Chemical Structure

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ABSTRACT: The diffusion of *n*-hexadecane (cetane) and *n*-dodecane, tagged in the terminal position by C^{14}, has been studied in trace amounts (<0.2%) by the thin smear method of Moore and Ferry in the following rubbery polymers: natural rubber, styrene–butadiene random copolymer (23.5% styrene by weight), several styrene–butadiene block copolymers, polyisobutylene, polydimethylsiloxane, and twelve polybutadienes with different microstructures, including 97% *cis*, 91.5% vinyl, 67% *trans*, and approximately half-*cis*, half-*trans*. The samples included uncross-linked polymers and samples cross-linked by dicumyl peroxide, sulfur, tetramethylthiuram disulfide, and (for polydimethylsiloxane) high-energy electrons. The diffusion coefficients (D) for the two penetrants were approximately in inverse proportion to their molecular lengths in several polymers. The diffusion of cetane showed the following behavior. (a) The apparent activation energy for diffusion at 25°, from the temperature dependence of D, was close to that for viscoelastic relaxation in most polymers but in natural rubber was smaller. (b) At 25°, D in different polymers covered a 2600-fold range from polydimethylsiloxane ($\log D = -5.80$, units square centimeters per second) to polyisobutylene ($\log D = -9.22$). With two exceptions, it followed the equation $\log D = A_d - (1/2.303f)$, where f is the fractional free volume derived from the temperature dependence of viscoelastic relaxation. For the polybutadienes, $\log D$ ranged from -6.34 (high *cis*) to -9.03 (high vinyl); it decreased slightly with increasing *trans* content at constant low vinyl. (c) Increasing cross-linking generally diminished D slightly. For natural rubber cross-linked by dicumyl peroxide, the change could be attributed to a decrease in free volume as proposed by Mason. (d) In styrene–butadiene block copolymers, D decreased with increasing styrene content but was larger than in a random copolymer with the same composition. The translational friction coefficient of cetane, ζ_1, calculated as kT/D, was similar in magnitude for most polymers to the monomeric friction coefficient ζ_0 calculated by matching viscoelastic data to the Rouse theory. A simple diffusion measurement may therefore serve to estimate the friction coefficient and hence the time and frequency scale of viscoelastic properties.

Diffusion of small molecules in concentrated polymer solutions and in essentially undiluted rubbery polymers has been studied to provide information about local segmental motions of the macromolecules.[1–9] The interpretation is simplest if the experiment corresponds to self-diffusion, as in the application of spin–echo nuclear magnetic resonance[4,7] or the use of a radioactively tagged solvent in a solution of constant composition.[1,5,6] An alternative is to use a radioactively tagged penetrant in trace amounts, so that its concentration remains very small during the course of the diffusion. This method (the "thin smear" method of Moore and Ferry[5]) has been employed in the present study to determine the diffusion coefficient of *n*-hexadecane (cetane) in a wide variety of rubbery polymers of different chemical structures and different degrees of cross-linking, together with some more fragmentary data on *n*-dodecane. The dependence of diffusion coefficient on temperature, cross-linking, and chemical structure is interpreted in terms of free volume, and the friction coefficients for translational motion of the penetrant molecules are compared with those of the polymer chains themselves derived from viscoelastic measurements.

(1) I. Auerbach, S. D. Gehman, W. R. Miller, and W. C. Kuryla, *J. Polym. Sci.*, **28**, 129 (1958).

(2) H. Fujita, *Advan. Polym. Sci.*, **3**, 1 (1961).

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(7) B. D. Boss, E. O. Stejskal, and J. D. Ferry, *J. Phys. Chem.*, **71**, 1501 (1967).

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Experimental Section

Polymers. Characterizations and sources of most of the cross-linked rubber samples have been given in previous publications on mechanical properties; the others will appear in forthcoming papers. These samples, furnished through the generosity of several colleagues, are identified here by the same code numbers that are used elsewhere. They include natural rubber (NR) cross-linked by dicumyl peroxide,[10,11] sulfur,[10,11] and tetramethylthiuram disulfide;[12] styrene–butadiene copolymer with 23% styrene (SBR), cross-linked by dicumyl peroxide;[13] 1,4-polybutadiene, *cis*:*trans*:vinyl = 40:53:7 (PB-*c,t*), cross-linked by dicumyl peroxide and sulfur;[14] *cis*-1,4-polybutadiene, *cis*:*trans*: vinyl = 96.5:1.9:1.6 (PB *cis*), cross-linked by dicumyl peroxide;[15] and polydimethylsiloxane (PDMS) cross-linked by high-energy electrons.[12,16] The uncross-linked polymers, polyisobutylene (PIB),[5] styrene–butadiene copolymer,[13] and 1,2-polybutadiene,[17] *cis*:*trans*:vinyl = 7:1.5:91.5 (PB-vinyl) have also been described elsewhere. In addition, a series of uncross-linked polybutadienes with various microstructure compositions was obtained from various sources. Relevant data will be given in a table below. Several styrene–butadiene block copolymers, prepared at the National Bureau of Standards by Dr. L. J. Fetters, were kindly furnished by Dr. Robert F. Landel. Data for their characterization will be given in a table below.

Penetrants. *n*-Hexadecane tagged with C^{14} in the terminal position was purchased in several lots from Nuclear-Chicago. The activity was usually 10.7 mCi/mmol. *n*-Dodecane similarly tagged was purchased from International Chemical and Nuclear Corp. Its activity was considerably smaller. Each sample was furnished in benzene solution. The solvent was removed by passing nitrogen over the solution and the radioactive hydrocarbon was diluted with the corresponding nonradioactive carrier (99% purity, purchased from Matheson Coleman and Bell). For most of the experiments the final activity was about 3 mCi/g, though all with *n*-dodecane and some with cetane were performed with solutions of considerably less activity providing correspondingly less precise results.

Procedure. The cross-linked samples were furnished in sheets from 0.04 to 0.09 in. thick. Disks of 1 in. diameter were cut with a stainless steel cutter attached to an electrically activated punch. Uncrosslinked samples were molded in somewhat larger disks from which 1-in. disks were subsequently cut. Two of these (uncross-linked styrene–butadiene and polybutadiene JSR-916) contained substantial gel fraction which was first removed by dissolving in benzene at a concentration of about 3%, straining out the gel, evaporating on a mercury surface, and removing the last traces of solvent under vacuum to constant weight.

The density of every sample (unless previously determined in connection with mechanical measurements[10-17]) was measured pycnometrically under water at 25°. In some cases measurements were also made at other temperatures to determine the thermal expansion coefficient. The disk thickness, essential for calculation of the diffusion coefficient, was then calculated from the mass, density, and diameter. In some cases this was checked satisfactorily by direct measurement with a micrometer, the sample being placed between two microscope slides.

Diffusion measurements were made by the thin smear method of Moore and Ferry[5] with minor modifications.[18] About 0.5–1 mg of radioactive penetrant was spread on the top surface of an aluminum cylinder 1 in. in diameter, with a stream of air from an empty plastic squeeze bottle. The cylinder was then mounted in a cylindrical cell and covered by the rubber sample disk, which was pressed gently with a spatula and covered by a 1-in. circle of aluminum foil 0.0002 in. thick. Finally, an aluminum ring with an inner diameter of 0.9 in. was placed over the foil. The foil prevents escape of traces of penetrant by vaporization, and the ring shields the counter from possible contributions by traces of penetrant which might have spread up the inner cylinder wall. The assembled diffusion cell was mounted under a Geiger-Müller tube (Model TGC-2, Tracerlab) and the entire assembly was kept in an air thermostat regulated to ±0.1° for the duration of an experiment. The tube was operated near 1400 V and was checked repeatedly with an uncalibrated radiocarbon source; it was connected to a scaler outside the thermostat (one assembly with Model 162, Nucleonic Instrument and Chemical Corp., and another with Model RCR2, Nucleonic Corp. of America). The background radiation was measured at the beginning of each experiment.

The sample and cell were usually allowed to come to temperature equilibrium in the thermostat before assembly. The temperature range was from 19 to 50° for cetane, 4 and 25° for dodecane. The moment of contact between the sample and the penetrant smear was taken as the start of the experiment. If the diffusion was rapid, counts were taken more or less continuously; if slow, intermittently, for long enough intervals to accumulate at least 1000 counts if possible. The center of each counting interval was taken as the corresponding elapsed time, and the activity was expressed as counts per minute during the interval.

Calculation of Diffusion Coefficient. Moore[19] derived an equation for the time dependence of the activity detected at the upper surface of the rubber disk and showed that if the thickness of the initial smear of penetrant is small compared to the rubber thickness, it is unnecessary to know the amount of penetrant applied. Moreover, if the absorption of β particles in the polymer is sufficiently high, the activity can be taken as proportional to the concentration of penetrant at the top surface and there results a very simple equation relating the time dependence to the diffusion coefficient, as used in previous work.[5]

In the present study, some of the samples were sufficiently thin so that finite contributions from below the top surface were taken into account, following the equation of Moore[19] (eq 1) where $N(t)$ and $N(\infty)$ are the activities detected above

$$N(t)/N(\infty) = 1 - 2[e^{-\pi^2\theta}/(1+\epsilon) - e^{-4\pi^2\theta}/(1+4\epsilon) + e^{-9\pi^2\theta}/(1+9\epsilon)\ldots] \quad (1)$$

the disk at time t and at equilibrium, $\theta = Dt/h^2$, $\epsilon = (\pi/\mu h)^2$, D is the diffusion coefficient, h the disk thickness, and μ the absorption coefficient in the rubber. Logarithmic plots of $N(t)/N(\infty)$ against θ for several values of ϵ, evaluated with an IBM 1620 computer, are shown in Figure 1. That for $\epsilon = 0$ is the function used previously.[5] To determine D, the counts per minute, $N(t)$, are plotted logarithmically against time and the points are matched to the curve with the appropriate value of ϵ. (The latter was estimated by taking

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(10) J. D. Ferry, R. G. Mancke, E. Maekawa, Y. Ōyanagi, and R. A. Dickie, *J. Phys. Chem.*, **68**, 3414 (1964).

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(14) E. Maekawa, R. G. Mancke, and J. D. Ferry, *J. Phys. Chem.*, **69**, 2811 (1965).

(15) J. F. Sanders, Ph.D. Thesis, University of Wisconsin, 1968.

(16) N. R. Langley and J. D. Ferry, in preparation.

(17) J. F. Sanders, J. D. Ferry, and R. H. Valentine, *J. Polym. Sci.*, in press.

(18) We are indebted to Dr. Robert S. Moore for suggesting some of these modifications.

(19) R. S. Moore, Ph.D. Thesis, University of Wisconsin, 1962.

Table I

Diffusion Coefficients of *n*-Dodecane and Cetane in Several Polymers

Polymer[a]	Sample code	Ref	Log *D*, cm²/sec Dodecane 4.1°	Dodecane 25°	Cetane 25°	Δ
NR	109-A₂-40	9	−7.55	−6.99	−7.12	0.13 ± 0.02
PB-*cis*	116-30	13	−6.63	−6.24	−6.34	0.10 ± 0.02
SBR	93-20	11	−8.30	−7.40	−7.55	0.15 ± 0.02
SBR	93-120	11	−8.50	−7.61	−7.72	0.11 ± 0.02
PIB	L-80	5	−10.07	−9.13	−9.22	0.09 ± 0.07

[a] NR = natural rubber, PB-*cis* = polybutadiene 96.5% *cis*, SBR = styrene–butadiene copolymer with 23.5% styrene, PIB = polyisobutylene.

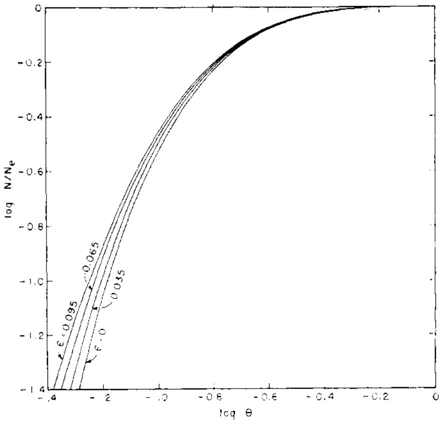

Figure 1. Activity measured at top of sample relative to equilibrium value, plotted logarithmically against θ in accordance with eq 1, for four values of ϵ as identified.

μ = 260 cm^{-1}, derived from the value[20] of 302 cm^{-1} for polystyrene, assuming μ to be proportional to the density; for most of the polymers studied here, the density is near 0.90 g/cm^3.) The abscissa origin of the theoretical curve corresponds to Dt/h^2 = 1, from which D is calculated. An example is shown in Figure 2. The precision depends largely on the counting statistics (limiting when the diffusion is rapid) and the accuracy with which the sample thickness h is known (limiting when the diffusion is slow, because thin samples must be used to avoid excessively long experiments). The best precision in log D was believed to be ±0.005. A detailed discussion of precision, with further details of apparatus and procedure, is given elsewhere.[21]

Since the equilibrium concentration of penetrant is always less than 0.2%, the diffusion coefficient D corresponds closely to the diffusion coefficient of penetrant[2,6] in essentially undiluted polymer.

Results

Comparison of *n*-Hexadecane and *n*-Dodecane. In Table I, log D is given for dodecane at 4.1 and 25° and for cetane at 25°, in five polymer samples. Units are square centimeters per second throughout. At a given temperature, D varies in different polymers by three orders of magnitude. At 25°, the difference Δ between log D for $C_{12}H_{26}$ and $C_{16}H_{34}$ is 0.12 for all the polymers essentially within experimental error (which is rather large here because of the low activity of the *n*-dodecane). This agrees with the ratio of molecular lengths (log 16/12 = 0.12) and suggests that the translational friction coefficient is directly proportional to length for these normal hydrocarbons. On this basis, the data for dodecane at 4.1° will be used in the discussion to estimate values at this temperature for cetane (which freezes at 18.1°).

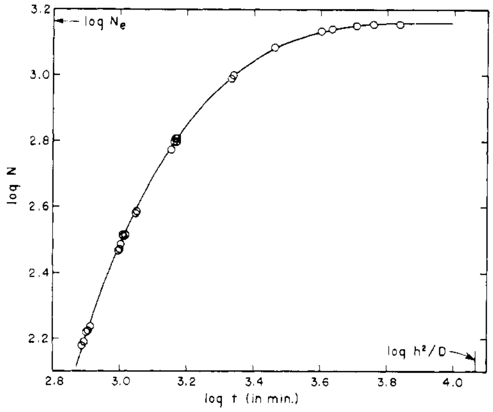

Figure 2. Activity in counts per minute plotted logarithmically against time in minutes, for cetane in natural rubber cross-linked with tetramethylthiuram disulfide (3.5%, vulcanized at 147° for 150 min), at 25.1°. Theoretical curve for ϵ = 0 matched with values of N_e and h^2/D as indicated.

Temperature Dependence for Cetane. Log D for cetane is plotted against reciprocal absolute temperature for several polymers in Figures 3, 4, and 5. For the limited temperature range employed, all plots except one are linear, and apparent activation energies for diffusion can be calculated from their slopes. Numerical values of D are tabulated elsewhere.[21]

Figure 3 shows natural rubber[9] samples with three different degrees of cross-linking and polybutadiene (*cis–trans*)[14] and styrene–butadiene[13] rubbers with two different cross-linkings. The latter is designated in the legend by ν, the moles of effective network strands per cubic centimeter, estimated from swelling measurements as quoted in the references cited. As in Table I, the diffusion coefficient depends greatly on chemical structure; it also decreases slightly with increasing cross-linking. The slopes are essentially independent of cross-linking except in the case of SBR. Figure 4 shows similar plots for polydimethylsiloxane[12,16] and *cis*-polybutadiene[13] with light cross-linking, and for an uncross-linked polybutadiene with comparatively high *trans* content. Figure 5 shows the same information for uncross-linked polyisobutylene and 1,2-polybutadiene.[17] The latter is nonlinear because of proximity of the temperature range to the glass transition temperature. The apparent activation energy at 25° has been calculated from the slope of a tangent.

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(20) F. Bueche, W. M. Cashin, and P. Debye, *J. Chem. Phys.*, 20, 1956 (1952).

(21) S. P. Chen, Ph.D. Thesis, University of Wisconsin, 1968.

TABLE II

APPARENT ACTIVATION ENERGIES FOR DIFFUSION OF CETANE AND FOR VISCOELASTIC RELAXATION

Polymer	Sample code	c_1	c_2	Ref for c_1, c_2	ΔH_a, kcal	ΔH_D, kcal
NR	98 H[a]	5.94	151.6	10	16.0	12.3 ± 0.5
	109-B$_2$-40	5.94	151.6	10	16.0	11.7 ± 0.5
	109-A$_2$-40	5.94	151.6	10	16.0	11.7 ± 0.5
	109-A$_2$-150	5.94	151.6	10	16.0	11.7 ± 0.5
PB-*c*,*t*	734	3.64	186.5	14	7.9	7.7 ± 0.4
	737	3.64	186.5	14	7.9	8.1 ± 0.4
SBR	93-20	4.57	113.8	13	16.4	12.8 ± 0.5
	93-120	4.27	107.6	13	16.3	14.1 ± 0.5
PDMS	A-2	1.94	217	22	3.6_5	4.4 ± 0.6
PB-*cis*	116-30	3.43	197.9	15	7.1	6.4 ± 0.4
PB-67% *trans*	EBR	3.96	171.4	*b*	9.5	11.2 ± 1.0
PIB	L-80	. . .	. . .	. . .	16.6[c]	16.4 ± 0.8
PB-vinyl	. . .	6.23	72.5	17	35.0	32.0 ± 1.0

[a] Not shown in figures; sample identified in ref 10. [b] Calculated as explained in connection with Table III. [c] From viscoelastic measurements near 25°: J. R. Richards, K. Ninomiya, and J. D. Ferry, *J. Phys. Chem.*, **67**, 323 (1963).

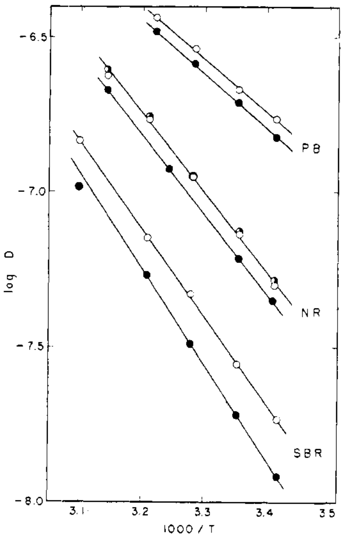

Figure 3. Log D of cetane plotted against $1000/T$ for three types of rubbers, identified by code numbers and (in parentheses) values of $\nu \times 10^4$: PB, polybutadiene,[14] *cis*:*trans*:vinyl = 43:50:7; ○, 734 (0.57); ●, 737 (2.37). NR, natural rubber:[11] ○, B$_2$-40 (0.54); ◑, A$_2$-40 (0.81); ●, A$_2$-150 (1.86). SBR, styrene–butadiene rubber:[13] ○, 93-20 (0.41); ●, 93-120 (2.50).

In Figure 5, points for the diffusion of cetane in polyisobutylene from Moore and Ferry[5] have been included. Although the polymer sample was the same, there is a discrepancy of the order of 0.2 log units. This is partly attributable to the fact that larger amounts of penetrant were used in the earlier work, causing some dilution of the polymer. The newer values are used in comparing with other polymers for the sake of consistency.

Values of $\Delta H_D[= RT^2(\mathrm{d} \ln D/\mathrm{d}T)]$ from Figures 3–5 are listed in the last column of Table II.[22] They are compared with apparent activation energies ΔH_a for viscoelastic relaxation calculated from the temperature dependence of relaxation times. The latter are obtained from the WLF constants c_1 and c_2, derived

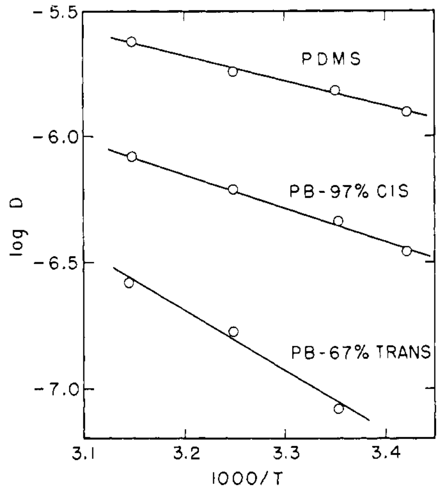

Figure 4. Log D of cetane plotted against $1000/T$ for three types of rubbers: PDMS, polydimethylsiloxane[12] (code A-2); PB-97% *cis*, polybutadiene with high *cis* microstructure[15] (code 116-30); PB-67% *trans*, polybutadiene with highest *trans* microstructure studied (code EBR).

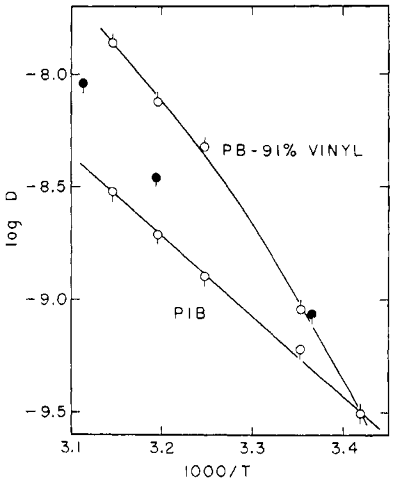

Figure 5. Log D of cetane plotted against $1000/T$ for two types of rubbers: PIB, polyisobutylene; PB-91% vinyl, polybutadiene with high vinyl microstructure;[17] ●, data for polyisobutylene of Moore and Ferry.[5]

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(22) A. J. Barlow, G. Harrison, and J. Lamb, *Proc. Roy. Soc.* (London), **A282**, 228 (1964).

Table III

Diffusion Coefficients for Cetane at 25° in Polybutadienes of Different Microstructures

Polymer code	Source	Microstructure, % *cis*	*trans*	vinyl	Log D at 25°	c_1	c_2	f at 25°
JSR-BRol	UR[a]	97	1.5	1.5	−6.38	3.41	198.9	0.128
116-30[d]	PPC[b]	96.5	1.9	1.6	−6.34	3.43	197.9	0.127
Taktene 1200	UR	97	1.5	1.5	−6.37	3.41	198.9	0.128
Phillips *cis*-4	UR	93	3	4	−6.40	3.46	196.2	0.126
JSR-ST-916	JSR[c]	77	20	3	−6.49	3.47	195.5	0.125
JSR-ST-917	JSR	61	36	3	−6.69	3.50	193.8	0.124
JSR-ST-918	JSR	45	51	4	−6.83	3.56	190.6	0.122
PB-740[d]	PPC	43	50	7	−6.66	3.64	186.5	0.119
PB-734[d]	PPC	40	53	7	−6.67	3.64	186.5	0.119
Diene 25	UR	36	53	11	−6.68	3.74	181.7	0.116
EBR	UR	19	64	17	−7.08	3.96	171.4	0.110
PB-vinyl	PPC	7	1.5	91.5	−9.03	6.23	72.5	0.069

[a] Uniroyal, courtesy of Dr. N. Tokita. [b] Phillips Petroleum Co., courtesy of Dr. G. Kraus. [c] Japan Synthetic Rubber Co., courtesy of Dr. K. Ninomiya. [d] Lightly cross-linked but not enough to affect D significantly.

Table IV

Diffusion Coefficients at 25° for Polymers of Different Chemical Structures

Polymer	Log D at 25°	T_g, °C	f at 25°
PDMS[a]	−5.80	−123	0.224
NR[a]	−7.12	−73	0.073
SBR[b]	−7.57	−63	0.095
PIB	−9.22	−68	0.073

[a] Extrapolated to zero cross-linking. [b] Uncross-linked sample, M = 100,000, 23.5% styrene by weight.[13] Extrapolation of data on dicumyl peroxide vulcanizates to zero cross-linking gives −7.55.

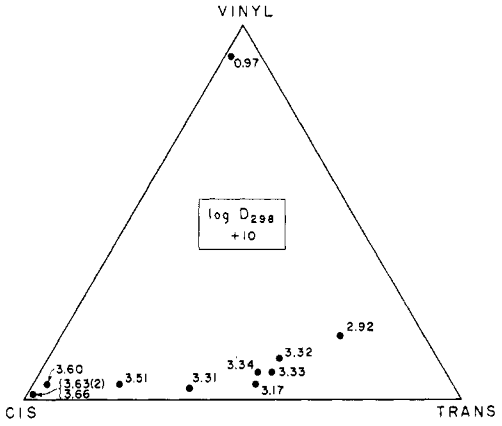

Figure 6. Log D + 10 of cetane at 25°, for various polybutadienes mapped against proportions of *cis*:*trans*:vinyl microstructure (data of Table III).

from temperature dependence of viscoelastic properties in the transition zone, by eq 2,[23] with constants based on

$$\Delta H_a = 2.303RT^2c_1/c_2 \qquad (2)$$

a reference temperature of 25°. For most of the polymers, ΔH_a and ΔH_D are identical within experimental error, although in natural rubber the temperature dependence for diffusion is distinctly smaller than for viscoelastic relaxation. The general agreement indicates that the molecular processes involving translatory motion of a foreign penetrant molecule and local rearrangements of the polymer segments themselves are closely similar. A more detailed comparison of the two processes can be invoked in terms of the free volume concept by examining the temperature dependence over a wider range; this is done for two of the polymers in the Discussion.

Dependence of Diffusion Constant of Cetane on Chemical Structure. One group of closely related structures is represented by the polybutadienes with different proportions of *cis*, *trans*, and vinyl microstructure. In Table III, twelve such polymers are listed with the laboratories from which they were obtained (not necessarily where they were manufactured) and their microstructures as reported to us, determined by infrared spectroscopy. Their molecular weights were all sufficiently high (>10^5) so the diffusion would not be expected to depend perceptibly on molecular weight. The values of log D at 25° are tabulated and are also mapped in Figure 6 on a conventional three-component diagram (added to ten to make all numbers positive). It is evident that D is largest for high *cis*-polybutadiene and decreases by about a factor of 2 for increasing *trans* content if the vinyl content remains low. (The *trans* content cannot exceed about 77% or crystallization occurs at room temperature.) For high-vinyl or 1,2-polybutadiene, however, D is smaller by nearly three orders of magnitude. This reflects the much slower molecular motions in the 1,2 polymer which are also apparent in viscoelastic measurements[17] and are primarily attributable to its high glass transition temperature. The remaining columns in Table III will be treated in the Discussion.

In Table IV, log D at 25° is tabulated for four other polymers, covering a range of 2600-fold. The relation of these values to free volume and viscoelastic behavior will be treated in the Discussion.

Dependence of the Diffusion Coefficient of Cetane on the Degree of Cross-Linking. It is evident from Figure 3 that progressive cross-linking decreases D slightly. Data are given in Table V for many samples of natural rubber vulcanized by three different cross-linking agents. As a measure of the degree of cross-linking, the moles of effective network strands per cubic centimeter, ν, is

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[23] J. D. Ferry, "Viscoelastic Properties of Polymers," John Wiley and Sons, Inc., New York, N. Y., 1961, p 225.

TABLE V

DIFFUSION COEFFICIENTS OF CETANE AT 25° in NATURAL RUBBER CROSS-LINKED TO DIFFERENT EXTENTS

Sample code	Cross-linking agent[a]	$\nu \times 10^4$ mol/cc	$\nu^* \times 10^4$ mol/cc	Log *D* at 25°
98 F	DCP	0.46		−7.13
98 G	DCP	0.62		−7.13
98 H	DCP	0.80		−7.13
98 I	DCP	1.20		−7.15
98 J	DCP	1.69		−7.19
109-A_1-20	DCP	0.47	0.11	−7.12
109-A_1-40	DCP	0.75	0.27	−7.15
109-A_2-40	DCP	0.81	0.30	−7.13
109-A_2-75	DCP	1.27	0.72	−7.16
109-A_2-150	DCP	1.86	1.30	−7.21
109-B_1-20	DCP	0.29	0.13	−7.13
109-B_1-40	DCP	0.58	0.25	−7.15
109-B_2-40	DCP	0.54	0.25	−7.13
109-B_2-75	DCP	0.88	0.49	−7.15
109-B_2-150	DCP	1.52	1.06	−7.19
74-30	S[b]	1.41[e]		−7.28
74-45	S[b]	1.73[e]		−7.31
74-60	S[b]	2.02[e]		−7.30
75-40	S[c]	2.24[e]		−7.37
76-15	S[d]	3.04[e]		−7.38
112-10	TMTD	1.15[e]		−7.200 ± 0.007
91–10	TMTD	1.55[e]		−7.201
91–150	TMTD	2.39[e]		−7.206

[a] DCP = dicumyl peroxide, S = sulfur, TMTD = tetramethylthiuram disulfide. [b] With diphenyl guanidine and mercaptobenzothiazole as accelerators: R. A. Stratton and J. D. Ferry, *J. Phys. Chem.*, **67**, 2781 (1963). [c] With benzthiazycyclohexyl sulfenamide as accelerator (see footnote *b*). [d] With mercaptobenzothiazole as accelerator (see footnote *b*). [e] From equilibrium compliance rather than swelling.

used; it is determined from equilibrium swelling measurements unless specified as determined from the equilibrium compliance. Both these methods involve somewhat arbitrary assumptions and the former tends to give values lower by 0.6–0.7 than the latter.[11,13,14] However, ν serves as a satisfactory comparative measure.

In Figure 7, log *D* is plotted against ν for dimethyl peroxide vulcanizates of natural rubber, *cis–trans*-polybutadiene, and styrene–butadiene rubber. The numerical data for the latter two are tabulated elsewhere.[21] The monotonic decrease in *D* with increasing ν is similar for all three rubbers, although for the polybutadiene there appears to be very little change at low degrees of cross-linking. For the natural rubber, differences in initial molecular weight from 2.3 to 7.7 × 10^5^ have essentially no effect on *D* or on its dependence on cross-linking. It may be inferred that the local rearrangements involved in diffusion are not affected by such a small concentration of free ends of molecules and the free volume associated with them. Nevertheless, the effect of cross-linking can be interpreted in terms of free volume, as shown in the Discussion.

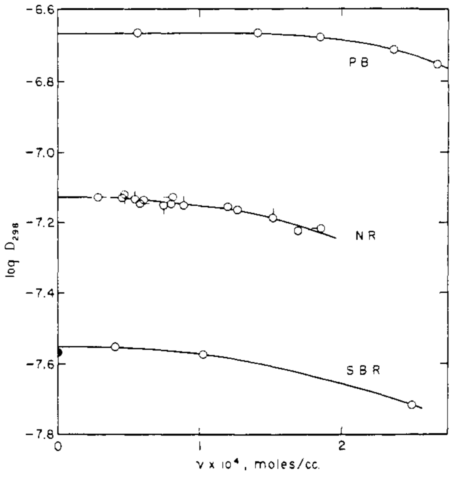

Figure 7. Log *D* of cetane at 25° plotted against moles of effective network strands per cubic centimeter derived from swelling measurements, for dicumyl peroxide vulcanizates of three types of rubbers identified as in Figure 3. Data for natural rubber from Table IV: ○, series 98. Pips denote different molecular weights in 109 series before cross-linking: ó, 2.3 × 10^5; o-, 2.6 × 10^5; ♀, 5.5 × 10^5; -o, 7.7 × 10^5; ●, uncross-linked SBR.

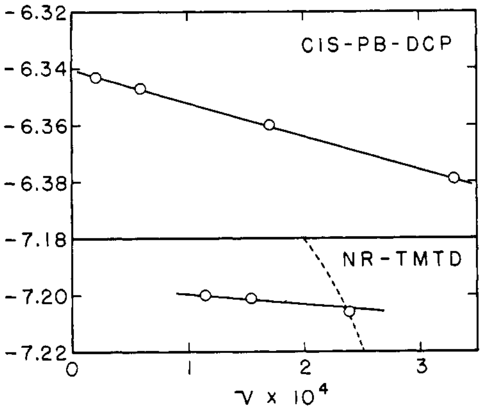

Figure 8. Log *D* of cetane plotted against moles of effective network strands per cubic centimeter derived from equilibrium compliance, for vulcanizates of two types of rubbers: top, high *cis*-polybutadiene cross-linked by dicumyl peroxide; bottom, natural rubber cross-linked by tetramethylthiuram disulfide. Dashed curve is corresponding relation for dicumyl peroxide vulcanizates of natural rubber, from Figure 7 (assuming[11] ν from compliance higher than ν from swelling by factor of 1.4).

The fragmentary data on sulfur vulcanizates in Table V have not been plotted, but show a more marked decrease in *D*, consistent with the effects of bound sulfur in reducing free volume and diminishing molecular mobility as seen in viscoelastic measurements.[10,24,25] The data for tetramethylthiuram disulfide vulcanizates are plotted with an enlarged scale in Figure 8; the dependence of *D* on ν is much less and hardly exceeds experimental error. This behavior may be associated with some chain scission accompanying cross-linking.[12] Also shown in Figure 8 are data for dicumyl peroxide vulcanizates of *cis*-polybutadiene (presented numerically elsewhere[21]); these follow the general pattern as do fragmentary data[21] on polydimethylsiloxane cross-linked by high-energy electrons (not shown).

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(24) A. R. Payne in "Rheology of Elastomers," P. Mason and N. Wookey, Ed., Pergamon Press, Ltd., London, 1958, p 86.

(25) H. D. Heinze, K. Schmieder, G. Schnell, and K. A. Wolf, *Kaut. Gummi*, **14**, 208 (1961).

Table VI

Diffusion Coefficients of Cetane at 25° in Styrene–Butadiene Block Copolymers

Sample code	Block type	—Molecular weight × 10^{-3}— Styrene	Butadiene	Density at 25°	v_B	Log D at 25°
5	SB	10.5	51	0.926	0.861	−6.85
4	SBS	10	50	0.942	0.745	−6.98
10[a]	SBS	9	32	0.961	0.674	−7.09
3	SBS	10.4	29	0.965	0.620	−7.11

[a] Not milled.

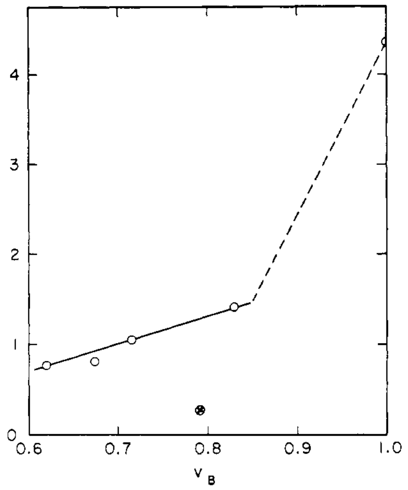

Figure 9. Diffusion constants of cetane in styrene–butadiene block copolymers at 25°, plotted against volume fraction of butadiene: ⊗, styrene–butadiene random copolymer.

Dependence of Diffusion Constant of Cetane on Composition in Styrene–Butadiene Block Copolymers. Diffusion coefficients of four block copolymers are given in Table VI. All but one (no. 5) were three-block polymers with styrene at the ends; all but one (no. 10) had been milled after synthesis. In Figure 9, D is plotted (linearly) against the volume fraction of butadiene, v_B. A point for *cis*-polybutadiene (average of several high-*cis* samples) is included at $v_B = 1$. The presence of the styrene domains diminishes D substantially, though not nearly as much as the corresponding proportion of styrene in a random copolymer, shown by the crossed circle for SBR of Table IV ($v_B = 0.791$). If the styrene domains represent impermeable regions, their effect can be attributed primarily to a decrease in the volume available for diffusion, but also to something analogous to cross-linking since the ends of the butadiene blocks are immobilized. No attempt is made at present to interpret the results quantitatively.

Discussion

Comparison with Diffusion of Smaller Hydrocarbon Molecules. Aitken and Barrer[26] studied the diffusion of smaller paraffins through natural rubber, lightly vulcanized with *t*-butyl peroxide, and obtained activation energies which increased somewhat with molecular size but are not very different from our values for *n*-hexadecane, suggesting that the activation energy approaches a limiting value with increasing length.

Table VII

WLF Parameters for Diffusion
(Reference Temperature 25°)

Polymer	Sample code	c_1^D	c_2^D	ΔH_D from c_1^D, c_2^D, kcal	B_d/B_a
NR	109-A$_2$-40	3.80	126	12.3	0.64
SBR	93-20	4.10	116	14.4	0.90
	93-120	4.10	116	14.4	0.96

Similarly, Prager, Bagley, and Long[27] studied sorption and desorption of *n*-butane and *n*-pentane in polyisobutylene at temperatures near our range and obtained ΔH_D as 16.7 ± 0.5 and 16.0 ± 0.5 kcal, respectively. For *n*-hexadecane we have 16.4 ± 0.8, again suggesting independence of length, implying that the unit process for diffusion is some kind of segmental motion. A similar conclusion is reached from the studies of Bresler[28] on tritium-tagged polyisoprene.

The magnitudes of D do not correlate quite so well. For *n*-butane and *n*-pentane in polyisobutylene, Prager, Bagley, and Long have $D = 1.30 \times 10^{-8}/n$, while we have for the longer paraffins $D = 2.07 \times 10^{-8}/n$, where n is the number of carbon atoms. Although the polymers may not have been identical in character, these comparisons suggest that the frictional resistance per unit length is somewhat larger for the smaller paraffins.

WLF Parameters. If the temperature dependence of diffusion is described by an equation of the WLF form[2] (eq 3), it should be possible to determine the coefficients

$$\log (D/D_0) = c_1^D(T - T_0)/(c_2^D + T - T_0) \qquad (3)$$

c_1^D and c_2^D from the intercept and slope of a linear plot[29] of $(T - T_0)/[\log (D/D_0)]$ against $T - T_0$, where D_0 corresponds to an arbitrarily chosen reference temperature T_0. Such a plot implies a wider temperature range over which plots such as Figures 3–5 are no longer linear. The limited temperature range imposed by the properties of cetane can be extended for two of the polymers, natural rubber and SBR, by including a point at 4.1° based on the assumption that Δ log D between cetane and *n*-dodecane at 25° (Table I) will have the same value at 4.1°. Thus, log $D_{4.1}$ (cetane) = log $D_{4.1}$ (*n*-dodecane) − Δ log D. WLF plots for these two polymers are shown in Figure 10; the two SBR vulcanizates cannot be distinguished here. The corresponding values of c_1^D and c_2^D are given in Table VII. Attempts to make similar calculations for the

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(26) A. Aitken and R. M. Barrer, *Trans. Faraday Soc.*, **51**, 116 (1955).

(27) S. Prager, E. Bagley, and F. A. Long, *J. Amer. Chem. Soc.*, **75**, 1255 (1953).

(28) S. E. Bresler, G. M. Zakharov, and S. V. Kirillov, *Vysokomol. Soedin.*, **3**, 1072 (1961).

(29) Reference 23, p 212.

other polymers in Table I were unsuccessful because of too much scatter. Values of ΔH_D calculated from these parameters by the analog of eq 2 are included; they are fairly close to those in Table II obtained by the alternative graphical method of Figure 3.

In the free volume interpretation of the WLF parameters,[2,29] $c_1^D = B_d/2.303f_0$ and $c_2^D = f_0/\alpha_f$, where f_0 is the fractional free volume at the reference temperature T_0, α_f is the thermal expansion coefficient of the free volume relative to the total volume, and B_d is a numerical parameter near unity, related to the minimum hole size for displacement of a segment of the penetrant molecule. The coefficients c_1 and c_2 from the temperature dependence of viscoelastic relaxation times (Table II) are similarly related to f_0 and α_f except that B_d is replaced by B_u, related to the minimum hole size for displacement of a polymer segment and commonly set equal to unity. It is clear that $c_1^D/c_1 = B_d/B_u$, and the last column of Table VII contains this ratio, calculated from c_1 of Table II. For SBR, B_d/B_u is close to unity; for natural rubber it is significantly smaller. This is of course consistent with the observation in Table II that natural rubber shows the greatest discrepancy between the apparent activation energy for diffusion of cetane and that for viscoelastic relaxation at 25°. Thus the cetane segment seems to move somewhat more freely in a natural rubber matrix than does a segment of the rubber molecule itself.

Correlation of Diffusion Coefficient of Cetane with Free Volume in Different Chemical Structures. The relation[2]

$$\log D = \log A_d - B_d/2.303f \qquad (4)$$

is based on analogy with the equation of Doolittle[30] and the theory of Cohen and Turnbull.[31] It has been used primarily to interpret the dependence of D on temperature (as above) and on concentration of diluent. However, to the extent that the constant A_d may depend primarily on the identity of the penetrant and not on the chemical nature of the polymer matrix, the magnitudes of D in different rubbers may be determined by their fractional free volumes; then log D should be a linear function of B_d/f with a slope of 1/2.303. For this correlation, values of f at 25° are included in Tables III and IV, calculated as $1/2.303c_1$, equivalent to setting $B_u = 1$. The WLF coefficients c_1 and c_2 in Table III were, in the case of PB-*c,t* and PB-vinyl, based on direct analysis of viscoelastic measurements.[14,17] The others were obtained by the following procedure. Glass transition temperatures were calculated from an equation of Kraus (personal communication) which related T_g to the contents of the three microstructures. Then, taking PB-*c,t* as a base, it was assumed for each polymer i that $c_2(\mathrm{i}) = c_2(\text{PB-}c,t) + T_g(\text{PB-}c,t) - T_g(\mathrm{i})$ and $c_1(\mathrm{i})c_2(\mathrm{i}) = c_1(\text{PB-}c,t)c_2(\text{PB-}c,t)$. This is equivalent to assuming that the free volume expansion coefficients α_f are the same for all the polybutadienes (their macroscopic thermal expansion coefficients are indeed closely similar[21]) and that the free volume f_g is the same for each polymer at its T_g. The value of f for PIB in Table IV is based on WLF coefficients assigned in ref 5.

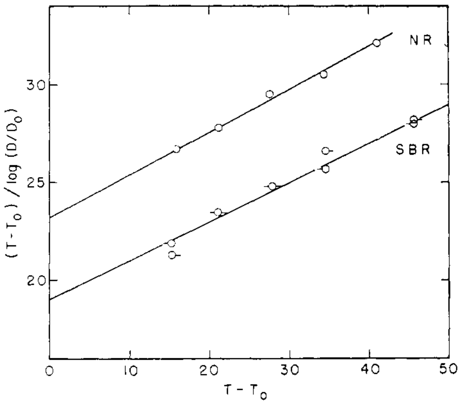

Figure 10. WLF plots for temperature dependence of diffusion of cetane: NR, natural rubber, A_2-40; SBR, styrene–butadiene rubber, ○-, code 93-20, -○, code 93-120.

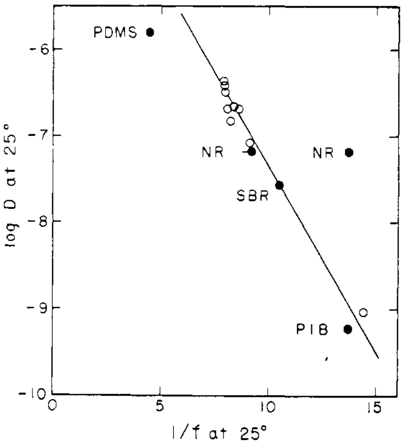

Figure 11. Logarithm of diffusion coefficient of cetane plotted against reciprocal free volume for different polymers: ○, polybutadienes with different microstructures; ●, other polymers, identified in Figures 3–5; -●, natural rubber, plotted against 0.64/f (see text).

Since B_d is not available, log D is simply plotted against 1/f in Figure 11. The points fall rather well on a line with the required slope. The point for natural rubber deviates but it conforms well if account is taken of its abnormally low value of B_d/B_a (Table VII) and the abscissa is plotted as 0.64/f. The point for polydimethylsiloxane represents a lower D than predicted but this polymer might be expected to be abnormal in view of its exceptionally high mobility; the internal resistance of the penetrant molecule itself to configurational changes may play a role in this case.

Interpretation of the Effect of Cross-Linking in Terms of Free Volume. In a study of natural rubber cross-linked by dicumyl peroxide, Mason[32,33] found that the temperature of maximum loss modulus at a frequency of 2 cycles/sec was increased by increasing cross-linking to the extent of 5×10^{-20} deg (cross-links/g)$^{-1}$. The glass transition temperature increased by the same amount, and the specific volume decreased. These results could be interpreted by assigning a decrease in free volume of 34 Å^3 per chemical cross-link or 20 cc/mol of cross-links.

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(30) A. K. Doolittle, *J. Appl. Phys.*, **22**, 1471 (1951).

(31) M. H. Cohen and D. Turnbull, *J. Chem. Phys.*, **31**, 1164 (1959).

(32) P. Mason, *ibid.*, **35**, 1523 (1961).

(33) P. Mason, *Polymer*, **5**, 625 (1964).

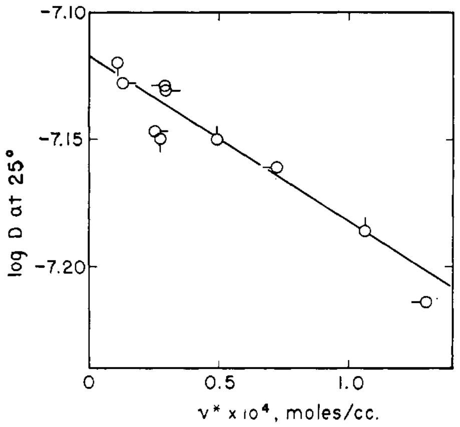

Figure 12. Log D of cetane at 25° plotted against estimated moles of network strands terminated by chemical cross-links for natural rubber data of Figure 7 (excluding 98 series), with same key for initial molecular weights.

The moles of chemical cross-links in our natural rubber vulcanizates of the 109 series can be roughly estimated by the equation of Mullins[34] (eq 5) where ν^*

$$\nu = (\nu^* + a)(1 - b)/\nu^*\overline{M}_n \qquad (5)$$

is the moles of network strands terminated by chemical cross-links (twice the moles of cross-links) per cubic centimeter and a and b are constants taken as 0.6 × 10^{-4} mol/cc and 2.1 g/cm^3, respectively. This equation should be modified for a more rigorous definition of entanglement trapping,[12,35] but it will serve for the present purpose, and values of ν^* thus calculated are included in Table V. In Figure 12, log D is plotted against ν^* and is found to be a linear function with a slope d log $D/\mathrm{d}\nu^* = -6.25 \times 10^2$. The corresponding decrease in free volume per cross-link can be calculated in the following manner.

From eq 4, d log $D/\mathrm{d}f = B_\mathrm{d}/2.303f^2$, so $\mathrm{d}f/\mathrm{d}\nu^* =$ (d log $D/\mathrm{d}\nu^*$)/(d log $D/\mathrm{d}f$) $= -6.25 \times 10^2 \times 2.303f^2/B_\mathrm{d}$; with $f = 0.073$ (Table IV) and $B_\mathrm{d} = 0.64$ (Table VII), we obtain −12 cc/mol of strands or −24 cc/mol of cross-links, in reasonable agreement with Mason's calculation.

Table VIII

Translational Friction Coefficients for Cetane and Monomeric Friction Coefficients for Segmental Motion

Polymer	Log ζ_1 at 25°, dyn sec cm^{-1}	Log ζ_0 at 25°, dyn sec cm^{-1}	$a \times 10^8$, cm
PDMS	−7.59	−8.05	6.2
PB-c,t	−6.73	−6.75	6.0
NR	−6.27	−6.41	6.8
SBR	−5.81	−6.11	6.7
PB-vinyl	−4.36	−4.11	7.5$_5$
PIB	−4.17	−4.35	5.9

Translational Friction Coefficients and Comparison with Monomeric Friction Coefficients of the Polymer Segments. The friction coefficient for translatory motion of cetane, ζ_1, in each polymer can be calculated from Tables III and IV by the relation $\zeta_1 = kT/D$. Values are given in Table VIII and show the expected wide range of magnitudes. These may now be compared with the friction coefficient per monomer unit, ζ_0, calculated from viscoelastic measurements by the usual procedure[36] of matching data to the predicted frequency dependence of the Rouse theory. The relaxation spectrum H can be used to determine the ratio $a^2\zeta_0/M_0^2$, where a^2 is the mean square end-to-end distance per monomer unit and M_0 is the monomer molecular weight; this ratio has been reported recently[17] for all the polymers listed except PDMS. To calculate ζ_0, the length a was estimated[21] from intrinsic viscosity data in θ solvents for the same or similar polymers; the values chosen are included in Table VIII. For SBR, M_0 was taken as the number average of the comonomers. For PDMS, ζ_0 was taken from the work of Lamb and collaborators.[22]

The values of ζ_1 are in the same order as those of ζ_0 (with one exception), and, surprisingly, they are very similar in magnitude, as noted earlier for the case of polyisobutylene.[5] The agreement in magnitude is a somewhat unexpected coincidence since n-hexadecane is much longer and has considerably greater molecular volume than any of the monomeric units. On the other hand, its two ends are free.

The correlation between ζ_0 and ζ_1 opens the possibility of predicting segmental mobility, and from it the time scale of all viscoelastic properties, from a comparatively simple diffusion measurement.

Acknowledgment. This work was supported in part by a grant from the National Science Foundation, and in part by the Research Committee of the Graduate School of the University of Wisconsin.

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(34) L. Mullins, *J. Appl. Polym. Sci.*, **2**, 1 (1959).

(35) R. G. Mancke, R. A. Dickie, and J. D. Ferry, *J. Polym. Sci.*, in press.

(36) Reference 23, p 255.