

Diffusion of Radioactively Tagged Penetrants Through Random and Block Styrene-Butadiene Copolymers and Filled *cis*-Polybutadiene

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Synopsis

The diffusion of radioactively tagged *n*-hexadecane in trace amounts has been studied in 22 random styrene-butadiene (SBR) copolymers with different styrene contents and butadiene microstructures; in several SBR block copolymers with different average block lengths (also diffusion of tagged 1,1-diphenyl ethane); in a triblock SBR copolymer cast from different solvents and also molded at elevated temperature; and in *cis*-polybutadiene filled to different extents with carbon black, calcium carbonate, and microglass spheres. The diffusion coefficient in random SBR copolymers decreased with increasing content of styrene and/or vinyl configuration and could be correlated with fractional free volume on the basis of linear additivity of the *cis*, *trans*, vinyl, and styrene moieties. In SBR block copolymers, the diffusion coefficient increased with increasing average block sequence length. For the triblock copolymer, the diffusion coefficient was approximately the same for samples molded or cast from solvents which are good for polybutadiene, but was far smaller for a sample cast from ethyl acetate, in which the polystyrene domains are probably lamellar. The effect of fillers on diffusion in *cis*-polybutadiene was compared with calculations on the basis of several theoretical models.

INTRODUCTION

The diffusion of radioactively tagged hydrocarbons in a molecular weight range near 200 through various rubbery polymers has been described in previous communications.¹⁻³ The results reflect the local chain mobility of the polymer matrix and its dependence on chemical structure, temperature, and presence of diluents; these features can be correlated to some degree with free volume. Such information can assist in predicting viscoelastic behavior, and is also relevant to problems of migration of extender oils⁴⁻⁶ and antioxidants and accelerators⁷ in rubber compounds.

The present paper describes additional results on three types of polymer systems: (1) random styrene-butadiene copolymers with different proportions of styrene and different butadiene microstructures; (2) block styrene-butadiene copolymer samples with different average block lengths and prepared by different casting procedures; (3) *cis*-polybutadiene containing various solid fillers.

EXPERIMENTAL

Random styrene-butadiene (SBR) copolymers were obtained through the generous cooperation of Drs. G. Kraus and H. E. Railsback of Phillips Petroleum

TABLE I
Characterization of SBR Random Copolymers and Diffusion Coefficients of *n*-Hexadecane

Code	Source ^a	wt % Styrene	Butadiene microstructure, %			$M_w \times 10^{-4}$	$M_n \times 10^{-4}$	ρ_{25}	Cross-linking ^b	log <i>D</i> (cm ² /sec)	<i>f</i> ^c
			cis	trans	vinyl						
49-308	P	23.9	44	46	10	13.9	12.0	0.936	ux	-7.069	0.101
49-309	P	24.6	29	42	29	15.6	12.9	0.938	ux	-7.427	0.092
49-310	P	19.8	45	44	11	16.7	10.5	0.930	ux	-7.088	0.104
49-311	P	40.4	44	45	11	16.2	13.9	0.964	ux	-7.724	0.089
49-312	P	0	40	49	11	24.0	12.6	0.895	ux	-6.672	0.118
49-313	P	23.9	44	46	10	13.9	12.0	0.936	x	-7.230	0.101
49-314	P	24.6	29	42	29	15.6	12.9	0.938	x	-7.724	0.092
49-315	P	19.8	45	44	11	16.7	10.5	0.930	x	-7.174	0.104
49-316	P	40.4	44	45	11	16.2	13.9	0.964	x	-7.884	0.089
49-317	P	0	40	49	11	24.0	12.6	0.895	x	-6.714	0.118
49-375	P	10.0	30	44	26	—	—	0.913	ux	-7.122	0.102
49-376	P	10.0	30	44	26	—	—	0.913	x	-7.291	0.102
50-403	P	15.0	40	48	12	32.5	16.0	0.921	x	-6.990	0.107
50-404	P	15.0	40	48	12	32.5	16.0	0.921	ux	-6.938	0.107
Stereon 700	F	21.0	40	52	8	—	—	0.932	ux	-7.032	0.104
Stereon 720	F	10.0	40	52	8	—	—	0.913	ux	-6.912	0.112
Stereon 750	F	19.1	30	59	11	—	—	0.928	ux	-7.050	0.104
Stereon 751	F	27.9	27	62	11	—	—	0.942	ux	-7.282	0.097
S-SBR	U	21.0	39	47	14	—	—	0.932	ux	-7.117	0.101
SBR-1500	U	23.5	10	75	15	—	—	0.936	ux	-7.550	0.098
Ameripol 1012	BFG	23.5	21	58	21	—	—	0.936	ux	-7.412	0.095
Ameripol 1513	BFG	40.0	11	69	20	—	—	0.963	ux	-8.187	0.085

^a P = Phillips Petroleum Co.; F = Firestone Rubber Co.; U = Uniroyal; BFG = B. F. Goodrich Chemical Co.

^b ux = Uncrosslinked; x = crosslinked.

^c Calculated from eq. (2).

Company; Dr. D. P. Tate of Firestone Rubber Company; Dr. N. Tokita of Uniroyal, Inc.; and Dr. B. L. Craig of B. F. Goodrich Company. Table I lists detailed information about their composition and characterization. The chemical compositions were determined by nuclear magnetic resonance spectrometry and butadiene microstructures by infrared spectrometry. The weight- and number-average molecular weights, M_w and M_n , were obtained from gel permeation chromatography. Certain samples from Phillips Petroleum Company were furnished both uncrosslinked and crosslinked. The latter had been crosslinked by heating with 0.75% dicumyl peroxide for 30 min at 153°C, in the form of sheets 0.7 to 1 mm thick. The uncrosslinked polymers from all sources were molded into sheets 1 to 2 mm thick, usually by pressing at 85°C for 3 hr at 5000 psi, followed by gradual cooling to room temperature. The disk-shaped samples used for diffusion measurements, of 1-in. diameter, were cut from the sheets by an electric punch.

A series of SBR copolymers with approximately constant styrene composition, butadiene microstructure, and molecular weight but with different numbers of alternating S and B blocks was generously provided by Dr. T. Kotani of the Japan Synthetic Rubber Company.⁸ These were crosslinked with 0.5% dicumyl peroxide for 30 min at 150°C in the form of sheets. The number of blocks was controlled by successive charges in the course of anionic polymerization. The composition and characterization of these samples are given in Table II, including the average sequence length of styrene units, \bar{n}_s , which ranges from 6 to 60.

A triblock SBR copolymer from Shell Chemical Company, Code TR 41-1648, was obtained indirectly in the form of a benzene-cast film from Professor N. W. Tschoegl of the California Institute of Technology and in bulk from Professor S. L. Cooper of the University of Wisconsin. The cis:trans:vinyl ratios of the polybutadiene moiety were 41:49:10, and the volume fraction of the polystyrene was 0.26. From the bulk polymer, additional films were cast by evaporation of other solvents: toluene, carbon tetrachloride, and ethyl acetate. The solvents were reagent grade; a 5% solution was allowed to evaporate on a leveled Teflon plate, constrained by a glass ring, and covered by a perforated sheet of aluminum foil, at room temperature. After one week, the film, about 1 mm in thickness, was evacuated at room temperature for an additional week. The thickness was uniform within 0.001 in. A film was also prepared from the bulk polymer by molding at 125°C for 5 hr.

Densities of all SBR copolymers, both random and block, were calculated on the basis of linear additivity of styrene and butadiene volumes, confirmed by pycnometric measurements on a few samples.

TABLE II
SBR Copolymers with Different Block Lengths

Code	No. of blocks		$M_n \times 10^{-4}$	wt % Styrene	\bar{n}_s	Butadiene microstructure, %			log D at 25°C (cm ² /sec)	
	S	B				cis	trans	vinyl	n -HXD	DPE
T-1	18	18	4.4	31.8	6	25.5	48.6	25.9	-8.201	-8.443
T-2	11	10	6.1	33.5	12	28.3	33.6	38.1	-7.766	-7.961
T-4	3	3	4.8	32.0	40	25.2	46.2	28.6	-7.545	-7.778
T-7	2	1	4.9	30.2	76	31.1	44.1	24.8	-7.287	-7.524
T-9	2	2	4.4	32.8	60	29.0	34.3	36.7	-7.165	-7.356

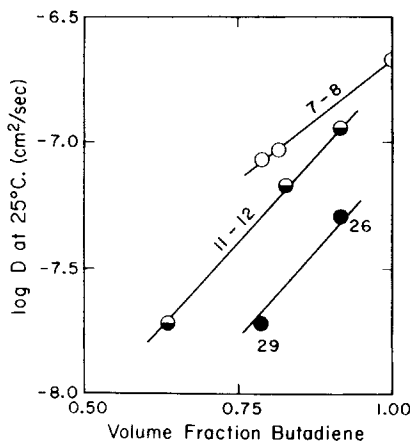


Fig. 1. Diffusion coefficient of *n*-hexadecane at 25°C through random SBR copolymers plotted against volume fraction of butadiene. Numbers refer to proportion of vinyl configuration in the butadiene moiety.

Finally, a series of filled samples of *cis*-polybutadiene was generously provided by Dr. I. Pliskin of Uniroyal, Inc. The fillers were HAF carbon black (average diameter 300 Å), graphitized HAF black, calcium carbonate (diameter 330–400 Å), and glass microspheres (diameter 4–5 microns). Sheets were molded between Teflon plates and removed from the mold at Dry-Ice temperature. Densities were measured by pycnometry under water.

The penetrants, *n*-hexadecane and 1,1-diphenylethane tagged with ^{14}C , were used as described previously.^{2,3}

Diffusion measurements were made by the thin smear method as described previously.^{2,3,9} The amount of penetrant was less than 1 mg. For such a small proportion of penetrant, the polymer is not significantly diluted and the experiment corresponds closely to one of self-diffusion of isolated penetrant molecules in a polymer matrix. All measurements were made at 25.00°C.

RESULTS AND DISCUSSION

Random SBR Copolymers

The logarithms of diffusion coefficients (D) of *n*-hexadecane at 25°C through 22 random SBR copolymers are listed in Table I. The values of D extend over a 60-fold range. As expected, they decrease with increasing content of either styrene or vinyl microstructure. These relations are illustrated in Figure 1, where $\log D$ is plotted against volume fraction of butadiene for three series (uncross-linked) with approximately equal vinyl microstructure contents. The effect of crosslinking is not prominent but tends to decrease D .

In previous communications,^{2,3} the diffusion coefficient through polymers of various chemical structures was related to the fractional free volume f by the equation

$$\log D = \log A_d - B_d/2.303f \quad (1)$$

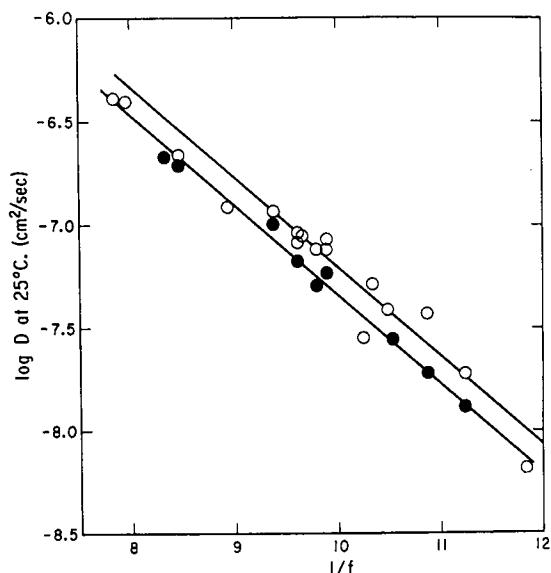


Fig. 2. Diffusion coefficient of *n*-hexadecane at 25°C through random SBR copolymers plotted against reciprocal of fractional free volume calculated from eq. (2). Open circles, uncrosslinked samples; black circles, crosslinked. Lines drawn with slope of $-1/2.303$.

where A_d and B_d are constants characteristic of the penetrant species, the latter being close to unity. For polybutadienes with several microstructures, f was calculated from temperature dependence of viscoelastic properties by use of the WLF equation, and rather good agreement was obtained² with eq. (1) for diffusion of *n*-hexadecane by setting $B_d = 1$.

For random copolymers with different styrene contents and butadiene microstructures, we now assume that the free volume is linearly additive in the weight fractions of the four constituents, so that

$$f = w_B(f_c c + f_t t + f_v v) + w_S f_s \quad (2)$$

where w_B and w_S are the weight fractions of butadiene and styrene in the polymer; c , t , and v are the mole (or weight) fractions of *cis*, *trans*, and vinyl configurations of the butadiene; and the f 's are the fractional free volumes corresponding to the pure species identified by the subscripts. The value of f_c at 25°C is taken as 0.128 from temperature dependence of viscoelastic properties for 97% *cis*-polybutadiene as previously assigned.² Those of f_t and f_v are obtained by applying eq. (2) without the styrene term to previous f values for polybutadienes of high *trans* and high vinyl; $f_t = 0.122$, $f_v = 0.063$. For the styrene, the pure polymer is of no help for evaluating f_s since it is below the glass transition at 25°, but by applying eq. (2) to the standard SBR for which data are well established ($f = 0.095$; $w_S = 0.235$; $c:t:v = 15:63:22$), we obtain $f_s = 0.045$. Values of f thus calculated from eq. (2) for all the polymers are listed in the last column of Table I.

In accordance with eq. (1), $\log D$ is plotted against $1/f$ in Figure 2, including four points from an earlier study,² and two lines are drawn with a slope of $-1/2.303$. There is some scatter, but the agreement is quite good, especially for the crosslinked samples. The uncrosslinked samples tend to have higher D by about

a factor of 1.8, which is rather large compared with the very slight effect of moderate crosslinking observed previously.² However, eq. (2) should serve for rather good predictions of D for random copolymers of any composition. Moreover, since D (or the friction coefficient ζ_1 calculated as kT/D) appears to be closely related to the monomeric friction coefficient ζ_0 which controls viscoelastic properties,² the position of the viscoelastic transition zone on the frequency scale can also be predicted.

SBR Copolymers with Different Block Lengths

The series of copolymers with different degrees of blockiness whose characterizations are listed in Table II was used for diffusion of both n -hexadecane (n -HXD) and 1,1-diphenylethane (DPE); the results are included in the table. The diffusion coefficient of 1,1-diphenylethane is consistently smaller by a factor of 0.58 to 0.65; previous comparisons showed a difference in the same direction.³ The most nearly random sample, T-1, has an average styrene block sequence of 6, and should be most nearly comparable with the random copolymers of Table I and Figure 2. On the basis of its fractional free volume calculated from eq. (2), $f = 0.074$, and $\log D$ of n -hexadecane should be about -7.9 ; a somewhat smaller value is observed. For all the other samples, $\log D$ is *larger* than calculated from the fractional free volume, and increases with average block length until D is larger by a factor of 10 for three- and four-block polymers. This is evidently associated with the formation of styrene domains leaving a butadiene matrix of much larger fractional free volume than the average and hence higher mobility. The geometric interference of impermeable styrene domains (impermeable because below T_g) affects the diffusion far less than does the decreased molecular mobility caused by random distribution of styrene units throughout the mass in the random copolymers. Such measurements might well serve to gauge the degree of blockiness in SBR copolymers by a very simple diffusion experiment.

Triblock SBR Copolymer

The diffusion coefficients of n -hexadecane in films of the triblock copolymer, cast from four different solvents and also molded, are included in Table III, together with a description of the domain structure as concluded for similar systems by Kraus, Rollmann, and Gardner¹⁰ from electron micrographs. The values are all nearly the same except for the film cast from ethyl acetate, for which D is smaller by nearly two orders of magnitude. This effect is undoubtedly due to a lamellar structure of the polystyrene domains when the casting solvent is much poorer for polybutadiene than for polystyrene, as discussed by Kraus¹⁰ and others; this material also has an abnormally high Young's modulus. This arrangement of the impermeable polystyrene domains almost but not quite completely blocks the diffusion. Molded material was deduced by Kraus to have polystyrene connectivity, but primarily in the flow direction; it does not impede the diffusion in our experiments.

The average $\log D$ for benzene-cast, toluene-cast, and molded films is somewhat smaller than that calculated for a polybutadiene with the given $c:t:v$ ratios, $\log D_0$, obtained from eq. (2) and Figure 2; $\log D_0 = -6.66$. Thus, $D/D_0 = 0.615$.

This represents a geometric structure factor associated with blocking by the unconnected polystyrene domains. It agrees moderately well with that predicted for impermeable spherical inclusions of various types of arrays, as discussed in the following section.

Filled *cis*-Polybutadiene

Before presenting the results of diffusion through filled polymer, we summarize the theoretical predictions of geometric structure factors for impermeable domains of various types as reviewed by Barrer.¹¹ The relative decrease in diffusion coefficient, D/D_0 , is related to the volume fraction of inclusions, v_1 , by the following equations:

1. Cubical particles in a simple cubic array:

$$D/D_0 = 1 - v_1^{2/3} \quad (3)$$

2. Spherical particles in a simple cubic array:

$$D/D_0 = \frac{2 - 2v_1 + (3\alpha/4)v_1^{10/3}}{2 + v_1 + (3\alpha/4)v_1^{10/3}} \quad (4)$$

where $\alpha = 1.31$.

3. Spherical particles in a body-centered cubic array:

$$\text{same as eq. (4), with } \alpha = 0.129 \quad (5)$$

4. Spherical particles in a face-centered cubic array:

$$\text{same as eq. (4) with } \alpha = 0.075 \quad (6)$$

5. Elongated ellipsoidal particles, one-third oriented parallel to each principal direction:

$$D/D_0 = \frac{1}{1 - (2v_1/3)} \times \left[1 - \frac{2v_1}{2 + (2v_1/3) - 0.306(2v_1/3)^4} \right] \quad (7)$$

In addition, Prager¹² has calculated the following relation for a random composite medium with certain plausible assumptions about interpenetration:

6. Random medium with certain plausible assumptions about interpenetration:

$$D/D_0 = \frac{(1 - v_1)[v_1 + (1 - v_1) \ln(1 - v_1)]}{2[v_1 + (1 - v_1) \ln(1 - v_1)] - (1/2)(1 - v_1)[\ln(1 - v_1)]^2} \quad (8)$$

TABLE III
Diffusion Coefficients of *n*-Hexadecane in Triblock Copolymer Films at 25°C

Code	Solvent	log D at 25° (cm ² /sec)	Domain structure ^a
48-B	benzene	-6.884	short fibrils
48-T	toluene	-6.883	short fibrils
48-C	carbon tetrachloride	-6.732	short fibrils
48-E	ethyl acetate	-8.684	lamellar
48-M	(molded)	-6.838	fibrillar with alignment

^a Based on description of similar systems by Kraus, Rollmann, and Gardner.¹⁰

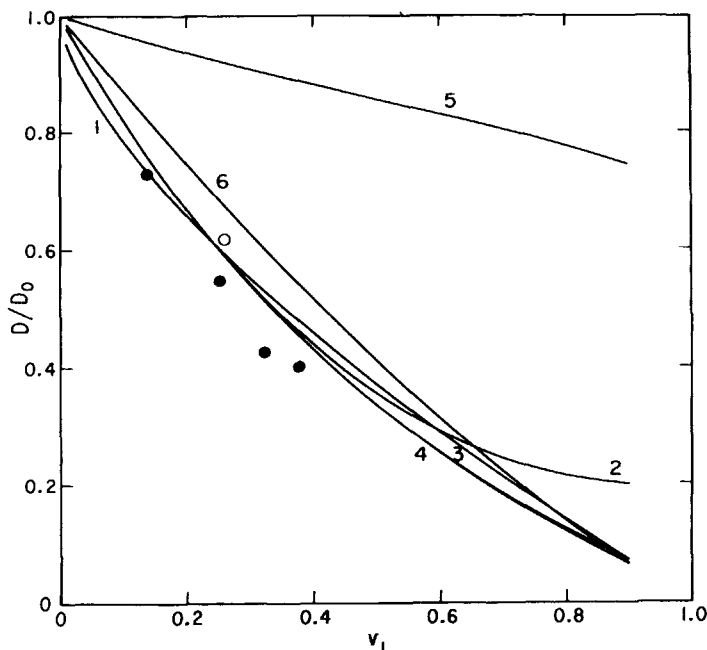


Fig. 3. Geometric structure factor D/D_0 plotted against volume fraction of impenetrable inclusions, for theoretical calculations numbered corresponding to text. Open circle is for block SBS copolymer (average of highest values in Table III); black circles, data of Chen for several block copolymers.

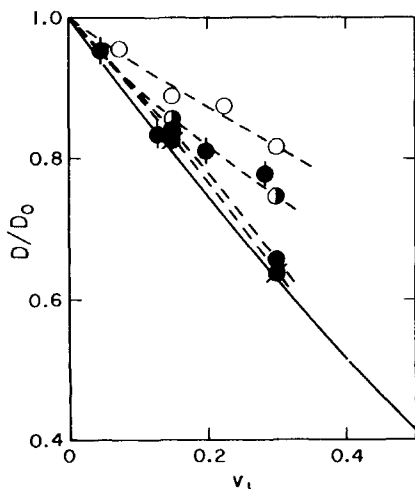


Fig. 4. Geometric structure factor plotted against volume fraction of filler for data of Table IV: (●) HAF carbon black; (●) graphitized HAF black; (●) carbon black, data of Deviney; (●) calcium carbonate; (○) glass microspheres. Solid curve is curve 6 from Fig. 3.

These structure factors are plotted against v_1 in Figure 3. Except for model 5, they do not differ much from each other. The open circle for the block copolymer systems, included in the figure, agrees rather well with models 1, 2, 3, and 4, but is below curve 6. Also included are several black circles from the data of Chen² on one SB (highest D/D_0) and three SBS block copolymers. The latter

TABLE IV
Diffusion Coefficients of *n*-Hexadecane in Filled *cis*-Polybutadiene at 25°C

Code	Filler type	ν_1	ρ	$\log D$	D/D_0
JF-0	unfilled <i>cis</i> -polybutadiene	0	0.895	-6.402	1.000
JF-1	HAF carbon black	0.15	1.043	-6.477	0.840
JF-2	HAF carbon black	0.30	1.184	-6.585	0.656
JF-3	graphitized HAF carbon black	0.15	1.052	-6.485	0.825
JF-4	graphitized HAF carbon black	0.30	1.196	-6.596	0.638
JF-5	calcium carbonate	0.15	1.203	-6.470	0.855
JF-6	calcium carbonate	0.30	1.422	-6.528	0.746
JF-7	glass microspheres	0.075	1.057	-6.423	0.955
JF-8	glass microspheres	0.15	1.129	-6.454	0.888
JF-9	glass microspheres	0.225	1.242	-6.461	0.873
JF-10	glass microspheres	0.30	1.358	-6.491	0.815

fall somewhat below all the theoretical curves. This discrepancy could be attributed to a rather thick interface between styrene and butadiene domains, constituting a volume of much lower permeability than that of pure butadiene. All the block copolymer data fall below curve 6, which may be the best theoretical representation for domains with sharp boundaries.

The diffusion coefficients D and structure factors D/D_0 are listed in Table IV for diffusion of *n*-hexadecane through *cis*-polybutadiene filled to different extents with carbon black, calcium carbonate, and glass microspheres. The results are plotted against ν_1 in Figure 4 together with the theoretical curve for model 6, the random structure. The carbon black data agree rather well with the model; the graphitized black is a little closer to theory, but the differences are small. The presence of bound rubber does not seem to influence the diffusion. Some earlier data of Deviney¹³ for radioactively tagged octadecane through polybutadiene at 100°C are presented for comparison; in these, the filler seems to have less effect, perhaps because of the higher temperature.

For the calcium carbonate, and even more so for the glass microspheres, the effect on D/D_0 is substantially less than predicted by model 6, *a fortiori* by models 1-4. This difference is probably due to the presence of voids associated with imperfect contact between the filler and polymer, which facilitate the diffusion.

This work was supported in part by a grant from the National Science Foundation. Some preliminary calculations were supported by the ARPA Materials Research Council Contract No. DAHC 15-71-C-0253 with the University of Michigan.

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Received January 22, 1976

Revised February 10, 1976