

## Diffusion of Radioactively Tagged Penetrants Through Rubbery Polymers. II. Dependence on Molecular Length of Penetrant

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### Synopsis

The diffusion of radioactively tagged *n*-hexadecane, *n*-dotriacontane, and a polybutadiene oligomer with molecular weight 1600 has been studied in 12 rubbery polymers. Diffusion coefficients were obtained from the theory for the thin smear method: for *n*-hexadecane and for *n*-dotriacontane (with one exception), in the form appropriate for a completely miscible polymer-penetrant pair, and for the oligomer in the form appropriate for slow entry of the penetrant across the penetrant-polymer interface. For the four flexible linear penetrants, *n*-dodecane, *n*-hexadecane, *n*-dotriacontane, and oligomer, the ratios of diffusion coefficients (or translational friction coefficients) are nearly the same in every polymer. It is concluded that these penetrants travel with similar segmentwise motions, although that is not the case with bulkier, more rigid penetrants. For the three normal paraffins, the friction coefficient is approximately proportional to molecular weight, but that for the oligomer is smaller than would be predicted on this basis.

### INTRODUCTION

The diffusion of certain radioactively tagged hydrocarbons through various rubbery polymers has been described in previous communications. Although the diffusion coefficient is primarily determined by the molecular mobility of the polymer, it depends to some degree on the size and shape of the penetrant molecule. For example, comparison of two linear paraffins, *n*-dodecane and *n*-hexadecane, showed the diffusion constant *D* to be inversely proportional to molecular length in several polymers where *D* ranged over three orders of magnitude.<sup>1</sup> For a bulkier molecule, 1,1-diphenyl ethane, the behavior is more complicated; the ratio of *D* for this molecule to that for *n*-hexadecane is not independent of the polymer but increases slightly with increasing *D*.<sup>2</sup>

The present paper describes results with two linear hydrocarbons of higher molecular weights: *n*-dotriacontane (C<sub>32</sub>H<sub>66</sub>, molecular weight 448) and a polybutadiene oligomer with number-average molecular weight 1600.

## EXPERIMENTAL

## Materials

The polymers were obtained through the generous cooperation of Dr. N. Tokita of Uniroyal, Inc.; Drs. G. Kraus and H. E. Railsback of Phillips Petroleum Company; Dr. P. Thirion of the Institut Français du Caoutchouc; Dr. E. T. McDonel of B. F. Goodrich Company; and Dr. Neil R. Langley of the Dow-Corning Corporation. They are identified in Table I together with code numbers, sources, and references to earlier papers<sup>3-5</sup> containing additional information about molecular weight, microstructure, etc. The samples for which this information has not appeared previously are described as follows.

The polybutadiene 44-735 had a cis:trans:vinyl ratio of 40:53:7 and an initial weight-average molecular weight of  $1.8 \times 10^5$ ; it was crosslinked with 0.11% dicumyl peroxide at 150°C for 45 min. Polybutadiene Taktene 1220 had a cis:trans:vinyl ratio of 98:1:1 and weight- ( $M_w$ ) and number-average ( $M_n$ ) molecular weights of 4.1 and  $0.9 \times 10^5$ , respectively. The ethylene-propylene terpolymer contained propylene, ethylene, and ethylidene neobornene in the weight ratios 39:57.7:3.3;  $M_w$  and  $M_n$  were 1.7 and  $0.7 \times 10^5$ , respectively. The poly(dimethylsiloxane) was a sample of high purity and very high molecular weight, with no content of  $M$  less than  $2 \times 10^5$  as indicated by gel permeation chromatography.

The uncrosslinked polymers 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.

The dilution and use of the penetrant *n*-hexadecane tagged with <sup>14</sup>C has been described previously.<sup>1,2</sup> *n*-Dotriacontane, tagged with <sup>14</sup>C, was purchased from Schwarz-Mann Company in cyclohexane solution. The solvent was removed by passing nitrogen gas over the solution, and the solid dotriacontane was dissolved in a small amount of *n*-decane as a relatively nonvolatile supporting liquid for the thin smear application to the polymer. The weight concentrations of two such solutions were 0.4% and 0.8%, and their specific activities were 0.56 and 0.96  $\mu\text{Ci}/\text{mg}$ , respectively. (The small effect of dilution of polymer by the *n*-decane was taken into account as described below.)

Tagged oligomeric polybutadiene for use as a penetrant was synthesized at the University of Akron as follows. High-vacuum procedures were employed. Sublimed *tert*-butyllithium was used as the initiator. Analysis of this initiator in perdeuterobenzene by an HR-300 spectrometer revealed that it contained no detectable impurities such as lithium hydroxide and lithium *tert*-butoxide. The polymerization of butadiene was performed in benzene at 25°C. The concentration of organolithium was  $10^{-3}$  molar ( $M$ ) so as to ensure that the resultant microstructures of the radioactive oligomer would be approximately cis:trans:vinyl = 40:50:10. The preparation of oligomeric polybutadiene is normally carried out at organolithium concentrations greater than  $10^{-2}M$ , which results in a polymer containing up to 50% of the 1,2 mode of butadiene addition.<sup>7,8</sup> The active chain ends were terminated in two steps. First, about 11 mg <sup>14</sup>CH<sub>3</sub>Br (purchased from ICN Corporation, specific activity 5 mCi/mM) was added to the polymerization vessel and the solution was maintained at 25°C for 48 hr. The

TABLE I  
Diffusion Coefficients at 25°C and Related Data

Polymer	Code	Source <sup>a</sup>	Data ref. <sup>b</sup>	log $D$ (cm <sup>2</sup> /sec)			log $\beta$ , sec <sup>-1</sup>	
				$n$ -HXD <sup>c</sup>	DTC <sup>d</sup>	DTC <sup>e</sup>		Olig. <sup>f</sup>
Polybutadiene	Diene 35	U	4	-6.667	-7.020	-7.036		
	49-312	P	3	-6.672			-7.316	2.0
	49-317	P	3	-6.714	-7.099	-7.115	-7.345	2.0
	44-735	P		-6.668 <sup>h</sup>	-6.976	-6.991		
Natural rubber	Taktene 1220	U		-6.364	-6.719	-6.732	-6.843	1.5
	NR-SS	U	4	-7.150	-7.468	-7.485		
SB rubber	NR-SMR	U	4	-7.131	-7.478	-7.495		
	A <sub>1</sub> -40	I	5	-7.122	-7.444	-7.461	-7.616	0.7
	S-SBR	U	3	-7.117	-7.440	-7.463		
	SBR-1500	U	3	-7.117	-7.856	-7.879		
Ethylene-propylene Poly(dimethylsiloxane)	EPDM	G		-7.442	-7.722	-7.744	-8.039	2.0
	PDMS	DC		-5.817	-6.024 <sup>g</sup>	-6.028 <sup>g</sup>		

<sup>a</sup> U = Uniroyal; P = Phillips Petroleum Co.; I = Institut Français du Caoutchouc; G = B. F. Goodrich; DC = Dow-Corning Corp.

<sup>b</sup> Reference for data on molecular weight, microstructure, etc.

<sup>c</sup> *n*-Hexadecane.

<sup>d</sup> Dotriacontane before correction for added diluent.

<sup>e</sup> Dotriacontane after correction for added diluent.

<sup>f</sup> Polybutadiene oligomer; case 3 theory of ref. 4.

<sup>g</sup> Case 2 theory of ref. 4.

<sup>h</sup> Datum from ref. 1.

remaining active chain ends were then terminated by the addition of nonradioactive methyl bromide. The termination reactions were done under vacuum. The radioactive oligomer was then isolated by distilling the polymerization solvent out of the polymerization reactor on the high vacuum line. The isolated oligomer was kept under vacuum until use.

The characterization of the radioactive oligomer was accomplished by use of Waters Ana-Prep gel permeation chromatography (GPC) instrument. The instrument was equipped with a seven-column Styragel set with a porosity range of  $2 \times 10^3$  to  $5 \times 10^6$  Å. The characteristics of this seven-column set have appeared elsewhere.<sup>9</sup> Solution concentrations of approximately  $\frac{1}{4}$  volume per cent were used at flow rates of 1 and  $\frac{1}{3}$  ml/min. The seven-column set was calibrated with the seven standard polybutadiene samples of narrow molecular weight distributions. The molecular weights of the samples ranged from 1300 to 53,000. The standard polybutadienes were synthesized and characterized at the University of Akron and the Lithium Corporation of America. A linear plot of  $\log \bar{M}_w$  versus elution counts was achieved over the molecular weight range of the polybutadienes used. Tetrahydrofuran was used as a carrier solvent and the Waters differential refractometer as a detector. Full-loop (2 ml) injections were made for both flow rates. A 5-ml siphon was used. No corrections for dispersion or column broadening effect were made for the weight-average and number-average molecular weights determined in this work. McCrackin<sup>10</sup> showed that these corrections were unnecessary for the analysis of GPC chromatograms obtained from the seven-column set used in this work. Also he calculated the  $p$  factor (which denotes the resolving power for a column set) for these seven columns to be 0.98 at the flow rate of 1 ml/min, while the value of  $p$  was nearly 0.99 at the slower rate. For ideal resolution,  $p$  is equal to 1, but  $p$  is less than 1 for real columns. Hence, the molecular weight averages obtained from the integration of the chromatograms should be corrected for the  $p$  factor. However, for the columns used in this work, the corrections were 1% and 2% for the slow and normal flow rates, respectively. Thus, in view of these minor corrections, no account of column broadenings was made for the GPC molecule weights reported herein. McCrackin's analysis and conclusions<sup>10</sup> were fortified by the good agreement between the values of  $\bar{M}_n$  and  $\bar{M}_w$  calculated from GPC chromatograms generated by this seven-column set and those determined from the absolute measurements on a series of mono- and polydisperse polystyrenes<sup>9</sup> and poly( $\alpha$ -methylstyrenes).<sup>11</sup>

The GPC chromatogram of the radioactive oligomer, obtained in tetrahydrofuran by the seven-column set at the flow rate of 1 ml/min, is shown in Figure 1. The number-average and weight-average molecular weights of the oligomer were 1600 and 1700, respectively. The number-average molecular weight of 1600 was in satisfactory agreement with the predicted value of 1500. There appeared to be about 4–5 weight per cent of high molecular weight material with a maximum molecular weight of 3500. This high molecular weight tail could be a product of either the polymerization reaction or a postpolymerization coupling reaction. The latter reaction would be expected to be free radical in nature since it is now recognized<sup>12,13</sup> that reactions between organolithium species and organic halide compounds can involve radical intermediates. Along this line, increases in molecular weight were reported<sup>14</sup> for the case where poly(butadienyllithium) was terminated by *sec*-butyl chloride. However, the presence of this high mo-

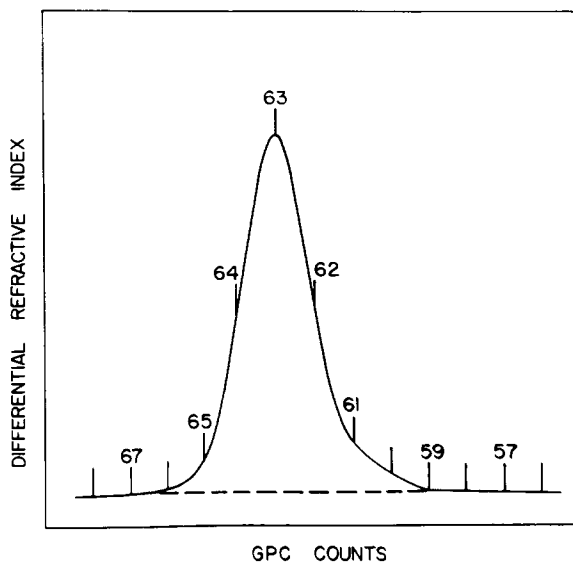


Fig. 1. GPC chromatogram of polybutadiene oligomer tagged by  $^{14}\text{C}$ . Flow rate, 1 ml/min; plate count, 750 ppf; concentration, approximately 0.25% in tetrahydrofuran; half-width, 2.0 counts.

lecular weight species is a minor deviation from a very narrow molecular weight distribution.

### Methods

Diffusion measurements were made by the thin smear method with automated data collection as described previously.<sup>1-3</sup> The amount of penetrant was approximately 2 mg. All measurements were made at 25.0°C.

### RESULTS AND DISCUSSION

As in previous studies,<sup>1-4</sup> logarithmic plots of the activity in counts per minute ( $N$ ), detected at the top surface of the polymer, against time ( $t$ ) were matched against theoretical plots of  $N/N_e$  against  $\theta$ . Here,  $N_e$  is the equilibrium activity observed after the penetrant is uniformly distributed through the polymer and  $\theta = Dt/h^2$ , where  $h$  is the thickness of the polymer disc. The data for  $n$ -hexadecane and  $n$ -dotriacontane were matched to theoretical curves appropriate to a polymer-penetrant pair miscible in all proportions (case 1 of ref. 4), except for  $n$ -dotriacontane in poly(dimethylsiloxane), for which the curve shape corresponded to case 2, appropriate to a penetrant with very low solubility in the polymer. The data for the polybutadiene oligomer corresponded to case 3, appropriate to conditions where the rate-determining step is entry of the penetrant across its interface with the polymer rather than the subsequent diffusion through the polymer volume. From these latter fits, the parameters  $\beta$  and  $C = (\beta h^2/D)^{1/2}$  were also determined;  $\beta$  is a measure of the rate of transfer across the penetrant-polymer interface. Values of  $D$ ,  $\beta$ , and  $C$  are listed in Table I.

The fact that diffusion of the oligomer corresponds to the theory for slow entry

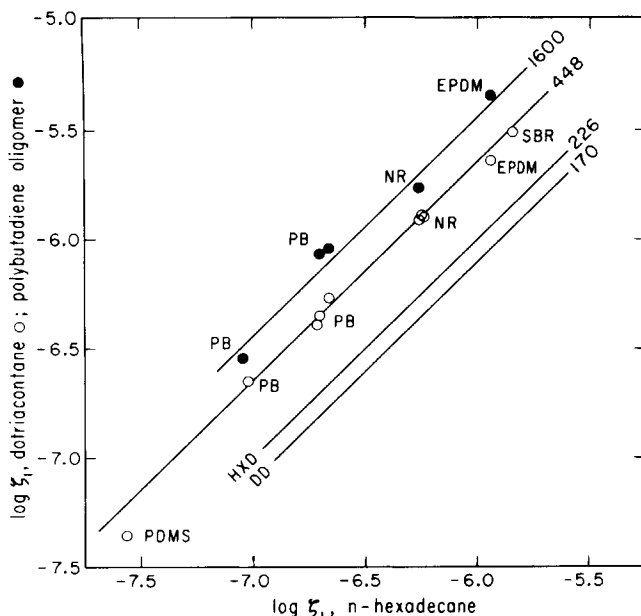


Fig. 2. Logarithms of translational friction coefficients of *n*-dotriacontane and polybutadiene oligomer plotted against the corresponding values for *n*-hexadecane, for various rubbers identified as in Table I. HXD, *n*-hexadecane (identity line); DD, *n*-dodecane from refs. 1 and 2. Numbers to right of lines are molecular weights.

across the polymer-penetrant interface is probably associated with its molecular weight being high enough to have very poor compatibility with polymers of different chemical composition. It is somewhat surprising that this is the case for the polybutadienes 49-312 and 49-317, since the microstructure of the oligomer is designed to be very similar to theirs (cis:trans:vinyl = 40:49:11), but it may be noted that  $\beta$  is much larger for these polymers than for the others; the characteristic time for crossing the interface,  $1/\beta$ , is 6 to 8 hr, compared with five to ten days for natural rubber and ethylene-propylene terpolymer.

The values of  $D$  for *n*-dotriacontane were subsequently corrected slightly for the diluent effect of the small amount of *n*-decane introduced with the radioactive penetrant. It was assumed that the decane would diffuse considerably faster than the dotriacontane so that the latter would be entering a slightly diluted polymer with diluent concentration  $0.002 \text{ g}/0.5 \text{ g} = 0.4\%$  by weight. This would increase  $D$  to an extent which can be estimated from the effect on the fractional free volume  $f$ , assuming that  $f = f_0 + \beta_f w_1$ , where  $f_0$  is the fractional free volume of the undiluted polymer,  $w_1$  is the weight fraction of diluent, and  $\beta_f$  is estimated<sup>15</sup> as 0.13. According to Fujita's free-volume treatment<sup>16</sup> of diffusion, based on the Doolittle equation, the increase in  $\log D$  is given<sup>15</sup> by  $(B_d/2.303)(1/f_0 - 1/f)$ . Values of  $f$  were estimated from data in the literature,<sup>1,16</sup> taking  $B_d = 1$ , with sufficient accuracy since the correction in  $\log D$  amounts to only 0.013 to 0.023. The corrected values are also given in Table I.

Diffusion coefficients for *n*-hexadecane have been previously reported for some of the same or very similar polymers,<sup>1</sup> and the new values are in excellent agreement.

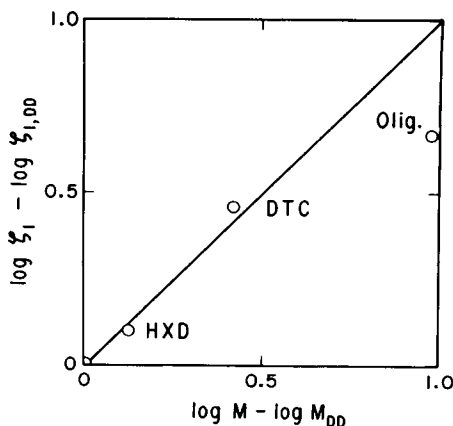


Fig. 3. Differences in  $\log \zeta_1$  from Fig. 2 plotted against differences in  $\log M$ , from dodecane as reference.

Comparisons of diffusion of different penetrants have previously been given in terms of the translational friction coefficient  $\zeta_1 = kT/D$ , where  $k$  is Boltzmann's constant and  $T$  is the absolute temperature. In Figure 2,  $\log \zeta_1$  for  $n$ -dotriacontane and the oligomer is plotted against  $\log \zeta_1$  for  $n$ -hexadecane. The results are close to lines of unit slope, so that  $\zeta_1$  ratio for any pair of penetrants is independent of the polymer over a range of magnitudes of  $\zeta$  (or  $D$ ) of more than a factor of 10. Lines for  $n$ -hexadecane (identity) and  $n$ -dodecane<sup>1,2</sup> are also included.

The slope of a line in Figure 2 comparing penetrant  $\alpha$  on the abscissa with penetrant  $\beta$  on the ordinate can be shown<sup>2</sup> to be equal to  $B_d^\beta/B_d^\alpha$ , where  $B_d$  is the coefficient of the Fujita equation<sup>5</sup>  $\ln D = \ln RTA - B_d/f$ . In the framework of the Cohen-Turnbull theory<sup>17</sup> as modified for a polymeric system,  $B_d$  is a measure of the open volume required for motion of a penetrant molecule or segment thereof relative to the volume of a polymer segment involved in a unit jump process; it is considered to be not far from unity but may depend on the size, shape, and flexibility of the penetrant. The unit slopes show that  $B_d$  is the same for all these linear penetrant molecules and indicates that they move segmentwise in a very similar manner. (For a nonlinear bulkier molecule, 1,1-diphenyl ethane, however,  $B_d$  was found to be perceptibly larger than for the linear flexible molecules.<sup>2</sup> By comparing the activation energies for diffusion and viscous flow, Park and collaborators<sup>17</sup> could deduce that for some other smaller bulky molecules such as dichloromethane, chloroform, benzene, and 2,2,4-trimethylpentane, diffusing in polybutadienes,  $B_d$  increased somewhat with molecular size; presumably, these molecules do not move segmentwise.)

The spacings between the lines in Figure 2 show the dependence of friction coefficient on molecular weight or length of the four linear flexible penetrants. This is illustrated in Figure 3, where  $\Delta \log \zeta_1$ , taking dodecane as reference, is plotted against  $\Delta \log M$ . The friction coefficient (in any polymer) is approximately directly proportional to  $M$  for the three paraffin hydrocarbons; but for the oligomer, it is considerably smaller than would be expected on this basis. Strictly, the comparison should probably be made on the basis of molecular contour length rather than  $M$ ; but calculations with bond angles and lengths

indicate that the molecular weight per unit length is nearly the same for a polybutadiene with the microstructure of the oligomer and for a normal paraffin. Possibly, incompatibility of the oligomer with the polymers is associated with a positive volume change of mixing which produces extra free volume in the immediate vicinity of the oligomer molecules, and this diminishes the friction coefficient and facilitates the diffusion. A similar suggestion can be made to interpret the abnormally low friction coefficient of *n*-dotriacontane in poly(dimethylsiloxane) which is evident in Figure 2.

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