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Polymer 44 (2003) 3061–3069

polymer

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Effect of penetrant size and shape on its transport through a thermoset adhesive: I. *n*-alkanes

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Received 22 August 2002; received in revised form 31 January 2003; accepted 5 February 2003

Abstract

The diffusion behaviors of a series of *n*-alkanes, ranging from C_6 to C_{17}, through a polyamide-type polymeric matrix have been investigated by means of mass uptake measurements. Since *n*-alkanes are known to display negligible interactions with the polymer matrix, this study serves to isolate the effects of penetrant size and shape on the transport process without undue interference from polymer–penetrant interactions. It is established that the diffusion of the *n*-alkanes through the polymer matrix studied is Fickian and proceeds via a Henry's law-type mechanism. The diffusion coefficients, D, are evaluated based on a thin-film approximation of the Fickian equation. The activation energies of diffusion, E_d, are determined from the temperature dependence of D, using the Arrhenius equation. Correlations between the Arrhenius terms, E_d and D_0, are also established which enable the prediction of diffusion coefficients for similar polymer–penetrant systems. It is also demonstrated by means of activation energy calculations and molecular simulations that the *n*-alkanes assume a linear geometry within the polymer matrix and diffuse along their long axes.

Keywords: Transport; Diffusion; Alkanes

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1. Introduction

Polymeric adhesives are currently utilized in an enormous variety of applications ranging from building construction and bonding of automotive panels to microchip encapsulants and flexible circuits for missile technology. However, many of these situations depend on the integrity of the materials over a substantial time. The lifetimes (durability) of the materials, in turn, are directly related to the environments to which they are exposed which may include, e.g., temperature and fluids (usually low molecular weight liquid penetrants). Such liquid penetrants may enter a polymer–substrate system via diffusion through the polymer matrix and/or cracks and crazes. Once a penetrant is introduced into a system, it may lead to a variety of chemical and physical changes in the material, some of which include solvent-induced crystallization [1,2] plasticization and swelling of the material [3,4] and/or creation of a weak boundary layer between the adhesive and substrate [5]. Most of these changes also alter the properties (including the mechanical behavior) of the polymer to a considerable extent and thereby may affect its performance. Therefore, it is essential in many applications to understand the nature of the diffusion of low molecular weight liquid penetrants into a given polymer matrix. This topic has been the focus of several investigations including a variety of studies that propose various models to describe the diffusion process [6–22].

We note that previously proposed diffusion models are not designed to accurately describe the diffusion process in terms of size, shape, and chemical nature of the penetrant. For example, many of the models were derived based on spherical molecular geometries; and thus, are usually applicable only to very low molecular weight penetrants. Also, the effects of specific interactions between the polymer and penetrant have often been ignored. Those diffusion models that do consider penetrant chemical nature often omit some of the other physical factors such as size and shape. Therefore, there exists a need to articulate a diffusion model encompassing the effects of all three variables—size, shape, and specific interactions between

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doi:10.1016/S0032-3861(03)00157-5

the penetrant and polymer. The current study attempts to first develop correlations that may form the basis of such a diffusion model. This is done by means of investigating the factors that influence the diffusion of low molecular weight liquid penetrants (such as *n*-alkanes and esters) into a polyamide-based polymeric adhesive. The parameters studied include external variables such as temperature as well as inherent molecular characteristics such as size, shape and chemical nature of the penetrants. The effect of the diffusion process on the resulting mechanical behavior of the polymer is also investigated and reported in a later paper in this series. In fact, the most significant and unique feature of this series of publications is the correlation between the chemical structure of the penetrant (and its transport properties) and the changes structural differences produce in the mechanical response of the polymer. These correlations enable the prediction of one of the above parameters, given a reasonable set of data on the other parameters. Such predictive capability linking molecular, diffusion and mechanical models can be generalized and extended to other, similar, polymer–penetrant systems.

Several experimental techniques previously have been used to study the solvent transport properties of a polymeric matrix [23–26]. Of these, the gravimetric or mass uptake method, although simple, has been demonstrated to yield reliable data [20,27–29]. In the present study, this method has been employed to monitor the diffusion of several low molecular weight penetrants through a polyamide-type polymeric matrix. The completed dynamic solvent uptake measurements have enabled the evaluation of the equilibrium and kinetic properties of the penetrant, which in turn are used to investigate the effects of molecular size, shape, and chemical nature of the penetrant on the transport process. The results from this investigation will be reported in a series of three publications mentioned above that focus on the following:

I. The role of penetrant size and shape on the diffusion of a series of *n*-alkanes into a polymer matrix.
II. The effects of penetrant size, shape, and chemical nature on the diffusion of a series of esters through a polymer matrix, and
III. Influence of the diffusion of the above penetrants (*n*-alkanes and esters) on the mechanical properties of the polymeric adhesive.

The current paper is the first in the series and addresses the role of penetrant geometry and molecular weight on the diffusion of *n*-alkanes through a rubbery matrix.

2. Experimental

The polymer utilized in the present study is a commercially available amorphous polyamide based upon poly-(ε-caprolactam) lightly crosslinked with low levels of Epon® 828 (diglycidyl ether of bisphenol-A). The material was cured at 100 °C for 1 h followed by postcure at 150 °C for 3 h. The glass transition temperature, T_g of the final cured material was determined by means of Differential Scanning Calorimetry (DSC). The polymer displayed a broad transition ranging from 20 to 43 °C.

A homologous series of low molecular weight aliphatic *n*-alkane penetrants ranging from hexane (C_6) to heptadecane (C_{17}) was used to investigate the transport properties of the polymer matrix. These materials (99.9 + % purity) were purchased from Aldrich Chemical Co. The molecular weights, molar volumes and solubility parameters of these fluids are listed in Table 1.

Rectangular pieces of the cured polymer film ($2.54 \times 1.27 \times 0.05$ cm) were cut for the dynamic solvent uptake measurements. These samples were weighed using an analytical balance and then placed into scintillation vials containing the different penetrants. These samples were stored for time up to 140 days at five test temperatures—23, 45, 55, 65, and 85 °C. At regular time intervals the polymer films were removed from the solvent, carefully wiped with Kimwipes® to remove excess solvent, and weighed using a microbalance. After each measurement the samples were promptly replaced in the solvent vials. The entire weighing process was completed in about 15–20 s. The solvent uptake was found by obtaining the change in mass of the films at different times, relative to the initial mass.

It is noted that the lowest test temperature (23 °C) falls within the broad glass transition temperature region of the neat polymer. However, the glass transition temperatures of the polymer samples saturated with the different penetrants were also measured by DSC, and it was found that the T_g's of the swollen polymer samples were depressed to temperatures up to 25 °C below the T_g of the neat polymer. As a result the polymer is physically in the rubbery state (not glassy state) at all of the test temperatures included in this study. This result is important in view of the fact that diffusion of penetrants through polymers usually follow different mechanisms (Fickian vs. non-Fickian) in the glassy state as compared to the rubbery state.

3. Results and discussion

The first step in the analysis of the sorption data acquired for the polymer–penetrant systems was to verify if the sorption process conforms to a known transport mechanism. In general, the mass uptake in polymer–penetrant systems has been demonstrated [30,31] to follow a power law expression of time of the form [28,30–33]:

$$\frac{M_t}{M_\infty} = Kt^n \tag{1}$$

where M_t and M_∞ are the experimental mass uptakes at times t and ∞, respectively; K, a constant dependent upon

Table 1
Physical characteristics of *n*-alkane penetrants

Penetrant	Solubility parameter ($MPa^{0.5}$)	Molecular weight (g/mol)	Molar volume (cm^3/mol)
Hexane (HX)	14.8	86.17	130.50
Heptane (HP)	15.2	100.20	147.40
Nonane (NN)	15.6	128.25	179.70
Decane (DC)	15.8	142.28	195.95
Undecane (UD)	16.0	156.30	212.47
Tridecane (TD)	16.4	184.35	244.92
Pentadecane (PD)	16.8	212.41	277.69
Hexadecane (HXD)	17.0	226.43	294.07
Heptadecane (HPD)	17.2	240.46	309.50

the structural characteristics of the polymer and its interaction with the solvent, and n, an exponent related to the transport mechanism, as follows:

$n = 0.5 \Rightarrow$ Fickian transport
$n = 1.0 \Rightarrow$ Case II transport
$0.5 < n < 1.0 \Rightarrow$ anomalous transport.

In accordance with Eq. (1), M_t/M_∞ of the penetrants from the present study were analyzed as a function of time. Nonlinear curve fitting (using a Levenberg–Marquardt algorithm) of the data up to 97% of the fractional uptake value was performed. The values of n and K for all the polymer–penetrant systems were evaluated from the curves. All the systems studied were found to exhibit n values ranging from 0.49–0.54 which is representative of a Fickian-type diffusion.

The Fickian nature of the sorption data was further verified from the reduced sorption plots for these systems, i.e. plots of M_t/M_∞ versus the square root of time normalized by the film thickness, $2L$. One such plot for the *n*-alkane penetrants at 45 °C is shown in Fig. 1. The curves in Fig. 1 display an initial linear increase with time$^{1/2}$ followed by a smooth approach to equilibrium represented by the plateau regions. The curves obtained at different test temperatures were found to be similar in shape and to possess the Fickian characteristic of linearity up to 60% fractional mass uptake ($M_t/M_\infty = 0.60$). This behavior can be attributed to the low T_g nature of the elastomeric polymer matrix and is typical of many rubbery polymers. The rapid segmental motions in such systems are characterized by short relaxation times and produce Fickian kinetics rather than more complex response[32].

Having confirmed the Fickian nature of the transport process, diffusion coefficients, D, were calculated using a 'thin-film' solution for the Fickian model of transport, the boundary conditions of which are

$T = 0$	$0 < x < 2L$	$C = 0$
$T > 0$	$x = 0,\ x = 2L$	$C = C_\infty$

where $2L$ is the film thickness, and C, the penetrant concentration in the polymer matrix at time t and distance x.

The first term approximation of a solution to the diffusion equation for short times [21,34] may be given by the expression:

$$\frac{M_t}{M_\infty} = \frac{2}{L}\left(\frac{D}{\pi}\right)^{1/2} t^{1/2} \tag{2}$$

Hence, the diffusion coefficient, D is related to the initial linear slope of the reduced sorption curves (Fig. 1) by:

$$D = \frac{\pi}{4}(\mathrm{Slope})^2 \tag{3}$$

Values of D for the *n*-alkanes at various test temperatures

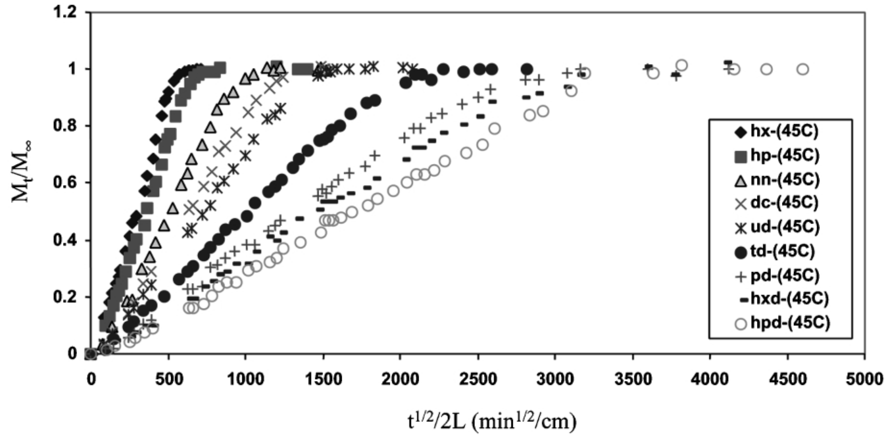

Fig. 1. Reduced sorption plots for *n*-alkanes at 45 °C.

were calculated from the initial slopes of the reduced sorption curves and are listed in Table 2. From these values it is seen that the diffusion coefficients decrease dramatically with increasing molecular weight of the *n*-alkanes. This may be attributed to the increasing geometric hole size requirement for the diffusion of the increasingly large penetrant molecules through the polymer matrix. The above result is consistent with previous studies that have demonstrated an inverse variation of diffusion coefficients with parameters such as number of carbon atoms, molecular weight, and molar volume that also describe the size of a penetrant [13,19,29,35–41]. Such a dependence of the diffusion coefficient, or diffusivity, on penetrant size has been previously [4,42] described by a power law expression of the form:

$$D = bM^a \tag{4}$$

where D is the diffusivity (cm^2/s); M, molecular weight of penetrant (g/mole); and b and a are material parameters.

According to Eq. (4), the experimental D values obtained at different test temperatures were analyzed as a function of penetrant molecular weight, M. Excellent fits ($R^2 > 0.99$) were achieved at all the test temperatures and confirm the applicability of the power law expression for the sorption of the *n*-alkanes into the polymer matrix. The parameters, a and b for our polymer–penetrant systems were evaluated. The values of a obtained fell between -4.7 and -2.1 for temperatures ranging from 23 to 85 °C, respectively, and are typical of aliphatic materials [43]. The increasing trend in the values of a with temperature is reflective of an increase in free volume and molecular mobility of the matrix at higher temperatures.

It is noted that the power law expression ignores any consideration of penetrant shape or isomerism while assuming that molecular mass is the major factor in governing transport behavior. We propose that the excellent match obtained between the expression and the experimental data is attributed to the homologous nature of the *n*-alkane penetrants series investigated and the negligible (or, at least, similar) attractions between the polymer and penetrants in these systems. Such a match does *not*, however, imply the validity of the power law expression in describing the diffusion process in all polymer–penetrant systems (including polar penetrants). This aspect will be addressed in greater detail in the following publication on the transport of polar ester penetrants through the same polymer matrix as in the present paper.

Table 2
Diffusion coefficients ($D \times 10^9$ cm^2/s) for *n*-alkanes as a function of temperature

Penetrant	Temperature (°C)				
	23	45	55	65	85
Hexane	12.3	37.1	67.9	92.2	[a]
Heptane	7.84	25.5	48.9	71.2	115
Nonane	2.79	10.8	23.9	37.7	61.1
Decane	1.69	9.05	16.2	28.6	52.4
Undecane	1.12	6.55	12.3	19.9	46.7
Tridecane	0.427	3.44	7.59	16.7	31.2
Pentadecane	0.211	2.13	4.27	8.32	23.9
Hexadecane	0.157	1.69	3.78	7.29	20.7
Heptadecane	0.111	1.29	2.58	6.21	17.1

[a] Data not obtained due to its low boiling point.

It was also found that the diffusion coefficients, D, increase with temperature for a given penetrant molecular weight. This result may be explained based on the greater free volume and associated mobility of the polymer with increasing temperatures. The temperature dependence of the diffusion coefficients has been analyzed in the present study based on the Arrhenius hole-formation model [44,45] given by the equation

$$D = D_0 \exp\frac{-E_\mathrm{d}}{RT} \tag{5}$$

where E_d, is the activation energy of diffusion (kJ/mole); D_0, Arrhenius front factor; R, the gas constant; and T, absolute temperature.

The activation energy, E_d is defined as the amount of thermal energy required to complete the transport of one mole of a diffusing molecule by creating openings between polymer chains large enough to permit their passage. Thus, E_d is a function of the inter- and intra-chain forces that must be overcome to generate this cavity. It follows that the E_d value will be greater for: (1) larger diffusants, (2) larger polymer matrix cohesive energies, and (3) more rigid polymer chains. Based on Eq. (5), linearized plots of log D vs. $1/T$ were constructed for all the polymer–penetrant systems studied. Values of E_d were obtained from the slopes of these plots and are depicted as a function of molar mass in Fig. 2. These E_d values are of the same order of magnitude as those typically reported for penetrant diffusion through a rubbery matrix [46], and are reflective of the increased mobility of the polymer segments that allow larger volumes to cooperatively participate in the transport process. As expected, the E_d values are also found to increase with penetrant size suggesting that more complex and even more

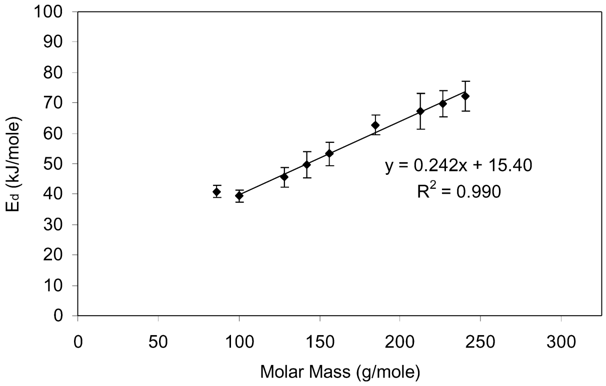

Fig. 2. Penetrant size dependence of the activation energy of diffusion, E_d, for *n*-alkanes.

cooperative segmental motions may be necessary for the diffusion of larger molecules [6,28].

It is also seen from Fig. 2 that the E_d values of the penetrants, with the exception of *n*-hexane, are linearly related to molar mass. The unique behavior of *n*-hexane may be suggestive of a critical size below which the penetrants diffuse via a simple “elemental” activation step. Above this size, additional activation energy may be required, reflecting a change to a more complex mechanism, or to one of higher cooperativity. This result is consistent with previous reports [47] on the diffusion of *n*-alkanes in polyolefins where a change in diffusion mechanism above a critical penetrant mass was reported.

The activation energy, E_d also displays a linear relationship with the Arrhenius front factor, log D_0, as can be seen from Eq. 5 (discussed below). Such a correlation has been experimentally verified for a number of polymers [25,26,44,47]. The linear dependence of log D_0 on E_d for the polymer/*n*-alkane systems examined in the present study is shown in Fig. 3. The slope of the straight line (0.121) is in excellent agreement with the value obtained by van Krevelen [43] for elastomeric materials.

It is noted that the kinetic relationships discussed in the above paragraphs (between molar mass of penetrant and E_d, and between E_d and D_0) can be used to predict diffusion coefficients for penetrant molecules similar to *n*-alkanes using the general form of the Arrhenius equation [6,43]. This can be done by:

1. Extrapolating the activation energy, E_d from knowledge of molecular size of the penetrant (using Fig. 2).
2. Determining corresponding D_0 from its dependence on E_d (using Fig. 3), and
3. Substituting the E_d and D_0 values from steps 1 and 2 above into Eq. (5) to determine the diffusion coefficient, D for the polymer–penetrant system at a given temperature.

It is important to mention that the values of D obtained using these steps are based only upon knowledge of the penetrant molecular weight, without the need for an extensive knowledge of other penetrant properties. Similar relationships have been obtained for the diffusion of hydrocarbon penetrants into a rubber.

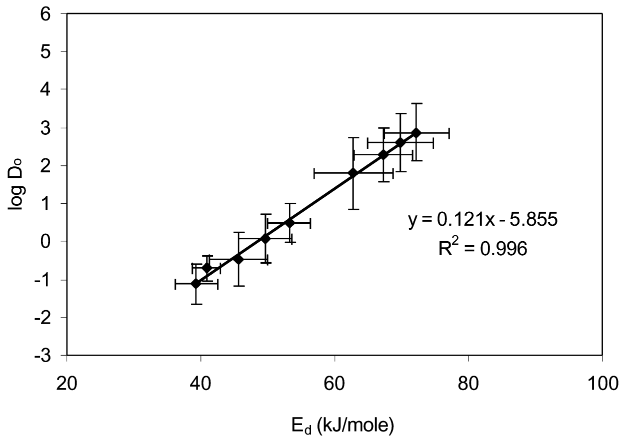

Fig. 3. Relationship between the Arrhenius diffusion front factor (D_o) and the activation energy of diffusion (E_d) for the *n*-alkanes.

Further insight into the mechanism of *n*-alkane sorption was gained by considering the equilibrium sorption values (i.e. solubilities) of the polymer–penetrant combinations. Equilibrium sorption may be defined as the equilibrium mass of penetrant absorbed per gram of the polymer, i.e. $M_\infty/M_{t=0}$. These values were directly calculated from the diffusion data described above for the polymer–penetrant systems and are listed in Table 3. An inverse dependence between solubility and molecular size (number of carbon atoms) of the penetrants is observed. This may be attributed to the fact that alkane sorption is an entropically driven process in this case [33]. Due to the aliphatic nature of these penetrants, only van der Waals and dispersion forces are involved in the guest/host intermolecular interactions, thereby limiting any enthalpic contributions. It is also seen from Table 3 that the equilibrium sorption values do not exhibit significant temperature dependence and this is indicative of low heats of solution. This is also reflective of the elastomeric behavior of the material [48] and may be explained as follows. In general, for an elastomer, an increase in temperature favors solubility, which in turn yields greater swelling and extension of the polymer chains. The free energy of the overall system decreases. However, there is a lowering of the configurational entropy of the polymer chains which is countered by an increased resistance to conformational change associated with the increased thermal energy. These two opposing effects may result in the negligible temperature dependence of the $M_\infty/M_{t=0}$ values observed.

The equilibrium sorption values discussed above may also be interpreted as thermodynamic equilibrium sorption constants designated as K_s. This constant is related to the thermodynamic enthalpy (ΔH_0) and entropy (ΔS_0) by means

Table 3
Equilibrium sorption values (% mass uptake) for *n*-alkanes at different test temperatures

Penetrant	Temperature (°C)				
	23	45	55	65	85
Hexane	9.09	9.13	9.20	9.28	[a]
Heptane	8.02	8.01	8.16	8.16	8.12
Nonane	6.81	7.20	7.29	7.26	7.06
Decane	6.27	6.62	6.75	6.70	6.46
Undecane	5.77	6.01	6.15	6.17	6.09
Tridecane	4.94	4.97	5.07	5.10	5.04
Pentadecane	3.95	4.07	4.19	4.20	4.26
Hexadecane	3.53	3.63	3.81	3.77	3.65
Heptadecane	3.38	3.35	3.59	3.43	3.45

[a] Data not obtained due to its low boiling point.

of the van't Hoff equation,

$$\text{Log } K_s = \frac{\Delta S_0}{2.303R} - \frac{\Delta H_0}{2.303RT} \quad (6)$$

As suggested by this equation, plots of log K_s vs. $1/T$ for all the polymer–penetrant systems were constructed. The ΔH_0 and ΔS_0 values were evaluated from the slope and intercept, respectively, of these plots, and are listed in Table 4. The values of ΔS_0 become increasingly negative with increasing penetrant size. This is due to the fact that the neighboring polymer chains must assume less probable conformations in order to accommodate a larger penetrant—thereby increasing the overall order of the polymer matrix [30,35] and resulting in a more negative ΔS_0.

ΔH_0 is a parameter that contains information regarding the type of sorption mechanism involved, e.g. a Henry's law type of sorption or a Langmuir (hole-filling) type of sorption. The Henry's law mechanism involves the formation of a vacant site requiring motions of polymer segments, i.e. an endothermic process, ($\Delta H_0 = \text{positive}$) followed by filling of this site by the solvent. A Langmuir type of sorption assumes that vacancies pre-exist in the polymer matrix and typically results in an exothermic process of solution ($\Delta H_0 = \text{negative}$). The ΔH_0 values for all the *n*-alkanes (from Table 4) are positive suggesting that a Henry's law type of sorption is involved. ΔH_0 values for these systems were also evaluated using an alternate method [9] involving permeability coefficients. The details of this method are not described here for purpose of brevity. However, it is noted that the ΔH_0 values from the two methods were identical, reaffirming the Henry's law mechanism of sorption for this elastomeric polymer/*n*-alkane study.

It is also noted that since the first term approximation to the solution of the diffusion equation at long times is analogous to the first order kinetic equation [49–51], it may be expected that the polymer–penetrant systems studied could also follow first order kinetics. This expectation has been confirmed in the present study from the excellent fits of the experimental data to the first order kinetic equation (results not presented here).

So far, it has been demonstrated that the diffusion of the *n*-alkane penetrants into the rubbery polymeric matrix is Fickian and proceeds via a Henry's law-type mechanism. The impact of molecular size (number of carbon atoms) of the penetrant on the diffusion coefficient and on the activation energy of diffusion has also been clearly established. In addition to molecular size, the diffusant shape as well as its chemical nature (polymer–penetrant interactions) is known to influence the transport of low molecular weight species [19,20,52]. However, due to the aliphatic, non-polar nature of the *n*-alkanes used in the present study, it is clear that the only interactions present in the system are van der Waals and dispersion forces. Therefore, the other predominant factor (in addition to molecular size) that could be influencing penetrant transport in such systems is molecular shape (geometry).

Small molecules such as simple gases and organic vapors are usually modeled in diffusion studies in terms of a spherical geometry, and their migration under our conditions would be presumed to occur utilizing polymer chain segmental motions. In the case of larger penetrants such as those in the present study, a spherical geometry cannot be assumed for a satisfactory model of behavior. Additional concerns regarding the creation of a vacancy necessary to accommodate such larger molecule in the polymer structure must be addressed. Under these circumstances, the average orientation assumed by the penetrant during transport is determined by the overall molecular conformations that would minimize the space requirements consistent with free energy barriers. It has been shown [29,36,40] that an extended geometry is favored in the transport of aliphatic hydrocarbons. This is due to the fact that such a geometry results in minimal perturbations of the polymer chain conformations required to form the vacant site.

In the present study, information regarding the shape of the *n*-alkane penetrants during the transport process was obtained by determining their activation energies (E_d) per methylene ($-CH_2-$) unit (E_d/CH_2-unit). This was achieved by using the difference between the E_d values for a pair of adjacent penetrants normalized by the difference in their number of methylene groups. The E_d/CH_2 values thus obtained for the *n*-alkane series are listed in Table 5. These values for C_9–C_{17} alkanes vary in

Table 4
Enthalpy, ΔH_0 (kJ/mol) and entropy of sorption, ΔS_0 ($\times 10^2$ kJ/mol/°K) for *n*-alkanes

Penetrants	ΔH_0	ΔS_0
Hexane	0.3870	−1.87
Heptane	0.2488	−2.01
Nonane	0.5838	−2.02
Decane	0.5363	−2.10
Undecane	0.8504	−2.07
Tridecane	0.3786	−2.37
Pentadecane	1.1150	−2.31
Hexadecane	0.6442	−2.55
Heptadecane	0.3727	−2.69

Table 5
Activation energy per addition of a methylene (CH_2) unit (kJ/mol/CH_2) for the *n*-alkane penetrants

Alkanes	
Number of carbons	E_d/CH_2-unit
9	3.1
10	4.1
11	3.5
13	4.7
15	2.2
16	2.4
17	2.4

the range 2.2–4.7 kJ/mole/CH_2-unit, and are consistent with those previously reported [26,52] values for the linear diffusion of saturated linear hydrocarbon chains parallel to their long axes. As a result it may be inferred that the *n*-alkanes in the present study diffuse in a similar fashion, i.e., linearly along their long axes. It is also noted from Fig. 2 that the E_d values of hexane (C_6) and heptane (C_7) are comparable within experimental error of experiment. We speculate that these two penetrants are below a critical molecular size, above which penetrant shape effects become significant.

Further support for the concepts discussed in the above paragraph is derived from a series of Monte–Carlo simulations using Macromodel® 5.0. The simulations were designed to determine the most probable energy conformations of a penetrant within an environment mimicking the polyamide matrix. These simulations were only executed for seven out of the nine *n*-alkanes studied. A complete description of the experiments and the analysis are available in the original work related to this paper [9]. The energy of each minimized conformation was used to interpret the plausibility of its existence and to estimate the range of energies necessary for those conformations. Due to the small energy differences among all the minimum energy conformations and the similarity in their estimated geometries, it was sufficient to use only the 20 lowest energy conformations from each simulation in the analysis. In addition, atomic distances were evaluated and, along with steric volume calculations, average descriptions of geometry in terms of an aspect ratio (defined as length/diameter, $L/2r$) were determined, and are listed in Table 6. The aspect ratio is a measure of the degree of linearity/non-linearity of a penetrant. It is seen from the table that the aspect ratios increase with increasing penetrant size. Furthermore, the deviation of aspect ratio from a value of one (i.e. perfect sphere) for the *n*-alkanes increases with increasing number of carbon atoms, indicative of higher degrees of linearity. The lowest molecular weight penetrant, *n*-hexane, displays an aspect ratio approaching the value of one, while still being linear. This is obviously due to the short length of this molecule with respect to its lateral dimensions. It was also shown earlier that the difference between the E_d values of *n*-hexane and *n*-heptane is negligible. Logically it may be inferred that the aspect ratio for *n*-heptane must also approach the value of one. Then, the above results (for *n*-hexane and *n*-heptane) are consistent with the above-discussed concept of a critical molecular size below which the penetrants diffuse via an ‘elemental’ activation step. It is also noted that a minor decrease in the aspect ratios of the largest molecular weight alkanes ($>C_{15}$) is observed. This suggests that these penetrants ($>C_{15}$) may have passed a molecular size limit where the long chains may fold back on themselves (while still being linear). Such an explanation is also supported by the high degree of flexibility of the methylene moieties.

Thus, it may be concluded from the above discussion that all the *n*-alkane penetrants appear to assume a linear geometry and diffuse along their long axes. An identical conclusion has been reached and widely reported by previous investigations based on sorption studies on a variety of polymer–penetrant systems [19,20,26,29,36,52]. Such a diffusion pathway based on ‘partially streamlined configurations’ [41], i.e. along the penetrant long axis, is not just limited to the sorption of a penetrant molecule through a polymer matrix. It has also been demonstrated [40,41] that the self-diffusion of low molecular weight species as well as within a given polymer matrix depend on molecular anisometry, and occur primarily via translations along the longest dimension of the low molecular weight species. It was important for later mechanical property/penetrant studies that the above concepts were established for our specific materials.

The result discussed above can now be used to justify the accuracy of a power law expression (Eq. (4) in describing the relationship between diffusivity and molar mass of these penetrants. It was mentioned that the excellent match of this expression with the experimental data could be due to the homologous nature of the *n*-alkane series. It is also known that this power law expression ignores any considerations regarding penetrant shape, isomerism, and mechanism of diffusion. Further, it may be argued that the excellent match of the Eq. 4 in describing the sorption data for the *n*-alkanes could also be due to the absence of significant differences among the shapes assumed by the penetrants during transport, namely linear, in addition to their homologous nature and the absence of polymer–penetrant interactions.

Table 6
Geometrical parameters obtained from Monte–Carlo simulations of *n*-alkane penetrants

Penetrant	Volume (Å^3)	Average radius (Å)	Average cross-section area (Å^2)	Average aspect ratio ($L/2r$)[a]
Hexane	113.6	2.354	17.46	1.409
Nonane	167.5	2.292	16.53	2.238
Decane	186.0	2.296	16.60	2.478
Tridecane	239.5	2.390	18.14	2.948
Pentadecane	270.5	2.450	19.16	3.163
Hexadecane	291.0	2.639	22.20	2.750
Heptadecane	308.5	2.708	23.48	2.780

[a] Length/diameter = $L/2r$.

In this paper, the effects of penetrant size and shape on the diffusion of a series of *n*-alkane penetrants through a polyamide-based polymer matrix have been discussed. Although similar results for a number of other polymer–penetrant systems are available in the literature, this is the first time that such a diffusion study on the present systems are reported to the knowledge of the authors. The significance of this work will become more obvious from the second and third publications, which address the effects due to the chemical nature of these same and new penetrants on their diffusion through the same polymer matrix as well as the correlations between the diffusion parameters and the changes in mechanical behavior of the polymer resulting from the penetrant diffusion, respectively.

4. Conclusions

The effects of penetrant size and shape on the transport behaviors of a series of *n*-alkane penetrants through a polyamide-type matrix have been investigated. Mass uptake measurements were used to study the transport process. It was established that the diffusion of the penetrants was Fickian and followed first order kinetics. It was also demonstrated from the sorption data that a Henry's law process was involved. The equilibrium solubilities were found primarily to be determined by the entropy of mixing as supported by the absence of specific interactions in the polymer–penetrant combinations. The solubilities of the penetrants were found to increase with decreasing penetrant size, and exhibited negligible variations with test temperature. The diffusion coefficients, D were evaluated based on a thin-film approximation of the Fickian equation. The D values were found to decrease with molar mass of the penetrants, and the variation was described by means of a power law expression. D was also found to increase with increasing temperature, and this dependence was modeled using the Arrhenius equation. The activation energies of diffusion, E_d were evaluated from the temperature dependence of D. E_d values were found to increase linearly with penetrant size, with the exception of *n*-hexane. Furthermore, correlations between the Arrhenius terms (E_d and D_0) were also established—these enable the prediction of diffusion coefficients at any selected temperature for similar polymer–penetrant systems.

The effect of penetrant shape on the transport behavior was examined by means of activation energy calculations and molecular simulations. All the *n*-alkanes were predicted to assume a linear geometry within the polymer matrix. Diffusion along their long axes is expected

The trends observed in the variation of the diffusion parameters were correlated to the size and shape of the penetrants.

Acknowledgements

The authors would like to thank Brett Kite for his assistance with the molecular simulations and members of the PolyPKem research group for valuable discussions. Additional thanks are due to the Naval Surface Warfare Center, the Center for Adhesive and Sealant Science, the Adhesive and Sealant Council, and the National Science Foundation for the funding of this project.

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