Diffusion of Gases Through Polyurethane Block Polymers

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Synopsis

The diffusivities of simple gases through a series of polyurethane block copolymers of differing aromatic urethane content and type of soft segment were measured using a quadrapole mass spectrometer as a detecting device. Although an Arrhenius expression generally described the temperature dependence of diffusion in this system, a discontinuity was observed in the Arrhenius plots for some materials, and the discontinuity was found to be related to the onset of the glass transition in the hard domains. Increasing the hard segment content of the materials decreased the diffusivity due to the increase in the activation energy of diffusion. Increasing the soft segment length brought about a decrease in the activation energy with an increase in diffusivity. Polyester urethanes had lower activation energies for diffusion than polyether urethanes of similar hard segment composition. Finally, as the penetrant diameter was increased, a decrease in the diffusivity and an increase in the activation energy was noted.

INTRODUCTION

Diffusion Studies

Many diffusion studies have been carried out in an attempt to obtain information and insight into polymer structure and molecular motion. The diffusion of simple gas molecules through polymer films is sensitive to changes in the polymer microstructure on a scale comparable to the size of the penetrant. The results of studies using gas molecules as "molecular probes" allow one to deduce the nature of certain changes in the polymer microstructure and the mobility of the polymer chains.

Diffusion through polymer membranes is adequately described by Fick's first law

$$J = -DS\frac{dP}{dx} \cong DS\frac{p_1 - p_2}{L} = P\frac{p_1 - p_2}{L} \qquad (1)$$

where J is the flux, D is the diffusion coefficient, S is the solubility coefficient, and $P = DS$ is the permeability coefficient. p is a partial pressure of the diffusing species.

The temperature dependence of the diffusion coefficient follows an Arrhenius relationship

$$D = D_0 \exp(-E_D/RT) \qquad (2)$$

where D_0 and E_D are the preexponential terms and activation energy for diffusion, respectively. The activation energy for diffusion is associated with the amount of energy required for hole formation against the cohesive energy forces

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of the polymer chains plus the energy needed to actually force the molecule through the polymer matrix. The preexponential term D_0 can be related to the number of holes or "looseness" of the polymer structure in the presence of the pentrant.[1]

Diffusion through heterogeneous polymeric materials is a more complex situation than the case of diffusion through a homopolymer. Consider the diffusion of a single penetrant species through a two-phase polymer system (e.g., a semicrystalline polymer). The diffusion process is complicated by the different modes of diffusion within each phase and by discontinuities across phase boundaries. Moreover, interactions between phases may influence the diffusion process, in principle, providing the basis for discontinuities and nonlinearities in the processes involved.

Determination of Diffusivities

A variety of experimental techniques have been developed to measure the parameters P, D, and S. Most diffusion coefficients have been measured using the high vacuum technique developed by Barrer.[2] This so-called time-lag method involves measuring the cumulative amount of gas which has passed through the membrane as shown schematically in Figure 1(a). The accumulation of the diffusing species is followed by noting the increase in volume in a receiving chamber kept at constant pressure[3-5] or a mercury manometer is used to measure the increase in pressure in a constant volume receiving chamber.[5-7] Brown and Sauber have developed a combined technique which measures an increase in pressure with corresponding increase in volume on the downstream side of the film,[8] and this method has been approved by the ASTM for measuring permeation and diffusion of plastic films (ASTM D1434-63).

The time-lag technique is not without difficulties,[4,9] however, and these experimental and analytical problems have led to the development of a number of flow techniques. The flow techniques differ from the time-lag methods in that they do not involve measuring the cumulative amount of gas $Q(t)$, which has crossed the membrane. Instead, the actual flux of gas $J(t)$ is measured, where $Q(t) = \int_0^t J(t)\, dt$. Analytically this corresponds to an alternate solution to the Ficks second law diffusion equation which has been given by Daynes[10] as

$$\frac{J}{J_s} = 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp\left(\frac{-n^2\pi^2 Dt}{L^2}\right) \tag{3}$$

where J_s is the steady-state flux. A convenient quantity which can be determined graphically from the $J(t)$ vs t diagram is the diffusion half-time $t_{1/2}$, when $J = \frac{1}{2}J_s$. This condition occurs when $\exp(-\pi^2 Dt_{1/2}/L^2) = 0.2539$.[11] Therefore,

$$D = L^2/7.199 t_{1/2} \tag{4}$$

A typical experimental plot is illustrated in Figure 1(b). In this work D was calculated using the half-time technique outlined above.

A number of detecting devices have been used with this flow technique[12-17] and the choice of detector is based primarily on the diffusing species and the anticipated rate of flux of those species. Because the polyurethanes were expected to be quite impermeable to simple gases, a mass spectrometer which is
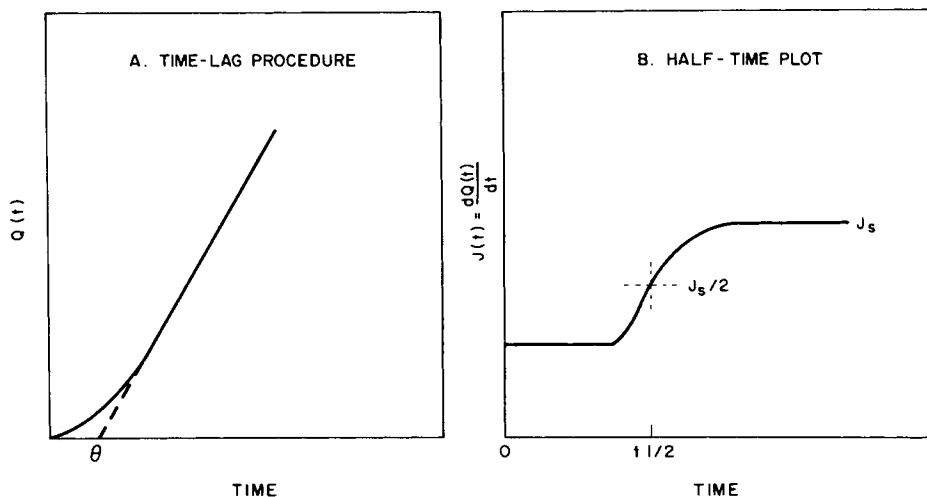
Fig. 1. (a) Time lag method for determining diffusion coefficients. (b) Half-time flow technique for measuring diffusion coefficients.

sensitive to very small quantities of gas seemed to be well suited to serve as the detector in this study.

The application of mass spectrometry to diffusion studies is not without precedent. Norton was the first to demonstrate the general applicability of mass spectrometry to diffusion studies.[18] Eustach and Jacquot made use of a mass spectrometer in their study of O_2 and CO_2 diffusion through very thick (0.25 in.) poly(vinyl chloride) films,[9] and reported that the mass spectrometer was ideally suited for the detection of the small fluxes involved. Saalfied and McDowell also successfully used a mass spectrometer to determine the permeability coefficient of each of the components of two and three component mixtures through thick sheets of neoprene.[19]

Polyurethane Block Polymers

Polyurethane block copolymers are heterophase systems composed of alternating aromatic urethane and macroglycol segments. The macroglycol segments are usually a polyether or a polyester. Since thermodynamic incompatibility between the chemically dissimilar blocks prevents formation of a homogeneous solution, the urethane and macroglycol segments cluster into separate domains and electron microscopy studies have confirmed the existence of two phases in this polymer system.[20]

The polyurethanes exhibit the major glass transition of each of their components. At ordinary temperatures, the macroglycol segments are above their glass transition temperature and are designated the soft segment; the aromatic segments which are below their glass transition temperature are designated the hard segments.

For convenience, the segmented polyurethane copolymers used in this study are identified by a code consisting of three parts such as ES-38-1 or ET-38-1.[21] ES refers to a segmented polyester-urethane while ET refers to a polyether-urethane copolymer. The 38 refers to the weight percent of diphenylmethane diisocyanate and 1 is the molecular weight of the soft segment times 10^{-3}. Thus,

ET-24-2 is a segmented polyurethane containing a 24 wt % hard segment and a repeating polyether soft segment which has a molecular weight of 2000.

The structure-property relations of the polyurethanes described above have been the subject of extensive investigation.[21-28] It has been found that the soft segments tend to aggregate into separate domains. At temperatures below the glass transition of the hard segments, the hard domains can act as filler particles and as crosslinks to restrain the motion of soft segment chains. This is the mechanism responsible for the enhanced mechanical properties of the materials. The effect of increasing the aromatic content is to further restrict the motion of the soft segments as the effectiveness of the crosslinking is enhanced while increasing the length of the soft segment serves to increase soft chain mobility. The mobility of the chains within the hard domains increases as the temperature is increased and the crosslinking effectiveness of the hard domains decreases. The effects of hard domain softening are apparent even at temperatures well below the hard segment glass transition.

There have been a limited number of diffusion studies utilizing polyurethane membranes. Schneider et al. studied the effects of structural variations upon water diffusion in polyurethanes.[29] The hard segments were composed of aromatic 4,4'-diphenyl-methane-diisocyanate (MDI) extended with butane diol. The soft macroglycol segments were chosen from poly(tetramethylene oxide) (PTMO), polypropylene oxide (PPO), poly(ethylene oxide) (PEO), or poly-butylene adipate (PBA). The soft segment segment molecular weight was 2000. For elastomers, there is often a linear relationship between the diffusivity and the quantity $T - T_g$. This suggests that the WLF equation, which represents the temperature dependence of viscosity (segmental mobility), also describes the temperature dependence of the diffusivity. Since the macroglycol segments are elastomers, it was thought that a plot of D vs $T - T_g$ would be linear. However, this was not the case. It was suggested that diffusion in polyurethanes is actually governed by an Arrhenius temperature dependence, although this was not verified. It was found that water solubility was nearly identical in all the samples. Schneider also found that water permeability was much lower in the PTMO and PPO polyurethanes than in the PBA polyurethane. From the temperature at which the glass transitions occur, one would expect the permeability to be greatest in PTMO. The permeability should be equal equal in the PBA and PPO materials. It was proposed that the degree of phase separation was greater in the PTMO and PPO polyurethanes than in the PBA polyurethane. The resulting greater number of hard domains (assumed to be essentially impermeable) served to produce a more tortuous route for the diffusing molecules. This resulted in a lower value for the diffusivity and, therefore, a smaller permeability coefficient.

Ziegel[30] studied simple gas diffusion in four different polyurethane materials. By making use of a model of segmented block copolymers in which the hard domains are assumed to be randomly dispersed as uniform spheres within a matrix of macroglycol elastomer, it was possible to decompose the diffusion curves for N_2, O_2, and Ar such that the diffusivity of the soft segments (D_s) could be distinguished from the diffusivity of the hard segments (D_h). At 30°C, the average ratio of D_s/D_h was 4.1.

EXPERIMENTAL

Apparatus

A schematic diagram of the apparatus is shown in Figure 2. An MS Gas Transmission Cell (Custom Scientific Instruments, Whippany, N.J.) was obtained and served as the membrane support structure and permeability cell. A UTI 100C quadrupole mass spectrometer served as the detector device and a getter ion pump with a speed of about 25 l./min provided the vacuum background for the mass spectrometer. The membrane was initially degassed using a mechanical roughing pump (Welch Model No. 140B) with a liquid-nitrogen (LN$_2$) cold trap (Perkin Elmer UI tec Model 233-1000) attached. A forced convection oven controllable to ±0.5°C was used to heat the membrane in those experiments conducted with the membrane above room temperature. The gases were dried over silica gel before entering the diffusion cell and the upstream pressure was regulated by a Mathison pressure regulator.

Procedure

The membrane in the diffusion cell was initially degassed by opening the two bellows valves (valves 1 and 2 in Fig. 2) and the three-way switching valve (valve 3) so that the membrane was exposed to the roughing pump. After approximately 6 hr, valve 2 was closed, isolating the downstream side of the membrane from the roughing pump and the high-vacuum valve into the mass spectrometer (valve 4) was gradually opened, exposing the downstream side of the membrane to the mass spectrometer. All of the membranes which were used were degassed for at least a total of 24 hr before a diffusion experiment was carried out. If the experiment was to be performed at an elevated temperature, the diffusion cell was heated for at least 60 min prior to the diffusion run.

At $t = 0$, valve 3 was switched so that the membrane was isolated from the roughing pump and exposed to the gas supply. (For most of the results reported here, the upstream gas pressure was maintained at 4.25 psig.) The length of time required to reach the steady state varied from 5 to 40 min and depended upon the particular membrane and temperature under consideration. Once steady state was reached the diffusion experiment was terminated and the cycle was repeated. No single membrane was used for more than 12 diffusion trials and, typically, the membrane was changed after every eight diffusion trials.
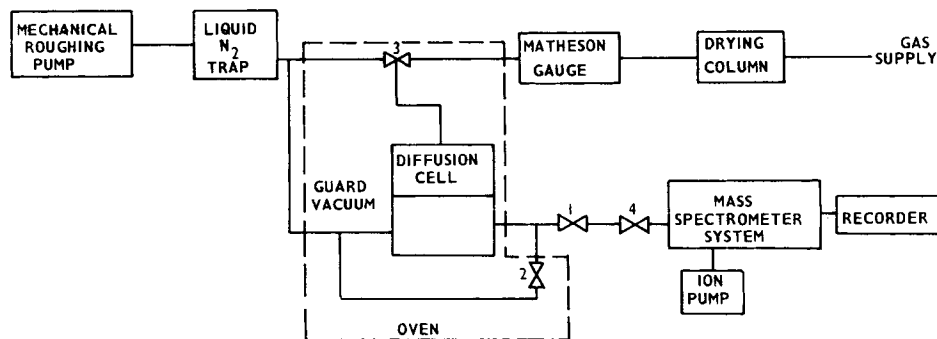

Fig. 2. Schematic diagram of the experimental apparatus.

Materials Studied

The polyurethane blocks copolymers were obtained from the B.F. Goodrich Chemical Company. The hard blocks of polyurethane segments were 4,4'-di-phenyl-methane diisocyanate (MDI). 1,4-butane diol (BD) served as hard segment chain extender. The soft blocks were either a polyether or a polyester. The polyether segment was polytetramethylene ether glycol (PTMEG) and the polyester segment was polytetramethylene adipate glycol (PTMA). Table I contains a chemical characterization of the polyurethanes studied.

Sample Preparation

The polyurethanes were prepared into films using the spin-casting technique described by Koberstein et al.[31] The membranes were all cast from 6% solutions. All spin-casting was done at room temperature. After being cast, the films were dried at 40°C for 24 hr in a vacuum oven. The membranes prepared in this way were between 0.006 and 0.009 cm thick. All of the polyurethanes were soluble in THF with the exception of ET-38-2 which was dissolved in DMF. In addition, a sample of ET-38-1 was prepared using DMF as a solvent in order to rule out any solvent effect. The results obtained with the two types of ET-38-1 (THF vs DMF) were identical indicating that there was no solvent effect in the preparation of these membranes.

RESULTS AND DISCUSSION

Diffusion experiments were carried out over a temperature range from room temperature to about 90°C. A number of different gases were used. The aromatic content, the soft segment length, the soft segment type, and the size of the penetrant molecule were varied. Table II lists the materials and the penetrants which were used. The effect of aromatic urethane content upon the diffusion process can be observed by comparing the results for the O_2-ET-38-1 with O_2-ET-28-1 and O_2-ET-31-1. The effect of soft segment length can be seen by comparing O_2-ET-38-1 with O_2-ET-38-2. A comparison between O_2-ET-38-1 and O_2-ES-38-1 will allow one to make conclusions about the effect of soft segment type. Finally, the effect of penetrant size can be seen by comparing O_2-ET-38-1, H_2-ET-38-1, and CO_2-ET-38-1 or by comparing O_2-ES-38-1 with CO_2-ES-38-1.

Figures 3–6 present the data plotted as $\ln D$ vs $1/T$. A linear relationship

TABLE I
Chemical Parameters of Diisocyanate Based Urethanes

Designation	Soft segment molecular weight	Wt. % MDI	Wt. % Hard segment	$x + 1$[a]	$\overline{M}_w \times 10^{-3}$	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$
ET-28-1	980	27.3	30.9	1.6	223	35.3	6.47
ET-31-1	980	31.2	36.6	2.0	274	107.0	2.58
ET-38-1	980	37.7	46.3	2.86	252	87.3	2.88
ET-38-2	2000	38.0	50	6	NA[b]	NA	NA
ES-38-1	901	38.6	47.6	3.11	236	32.4	7.28

[a] $x + 1$ denotes the average number of diisocyanate residues per hard segment.
[b] NA, not available.

TABLE II
Materials and Penetrants Used in this Study

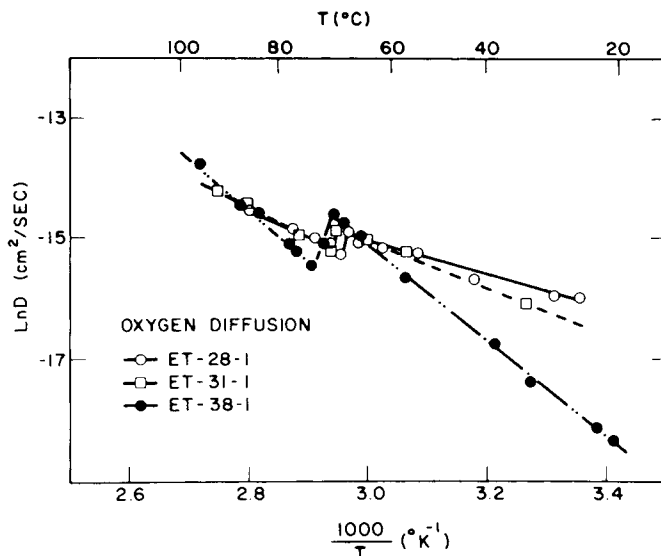| Material	Penetrant
ET-38-1	O_2, CO_2, H_2
ET-31-1	O_2
ET-28-1	O_2
ET-38-2	O_2
ES-38-1	O_2, CO_2

Fig. 3. Arrhenius plot for oxygen diffusion through ET-28-1 -O-, ET-31-1 -□-, and ET-38-1 -●-.

between $\ln D$ and $1/T$ indicates that the Arrhenius expression adequately represents the temperature dependence of diffusion for the system under study. It can be seen that in general the Arrhenius expression is valid but that over certain small temperature ranges a discontinuity appears in some of the data, and is best represented by two straight lines in these cases. Table III lists the diffusion coefficient for each gas-membrane pair at 30°C. It is apparent that the magnitude of the diffusivity is sensitive to each of the parameters which were varied. The following trends may be seen: (1) an increase in the aromatic content results in a decrease in the diffusion coefficient; (2) an increase in the segment length produces an increase in the diffusion coefficient; (3) an increase in the size and the penetrant results in a decrease in the diffusion coefficient; and (4) The polyester urethane has a larger diffusion coefficient than the polyether.

It should be recalled that these are heterogeneous polymer systems made up of an interpenetrating domain structure. This implies that the value of the diffusion coefficients listed in Table III reflects contributions from each of the phases in the material. In this particular polymer system at 30°C, the hard domains are about 50 deg below their T_g, while the soft domains are about 70 deg above their T_g. It seems likely that the diffusion coefficient would be lower in the glassy hard domains than in the soft domains. In the O_2 and poly(vinyl
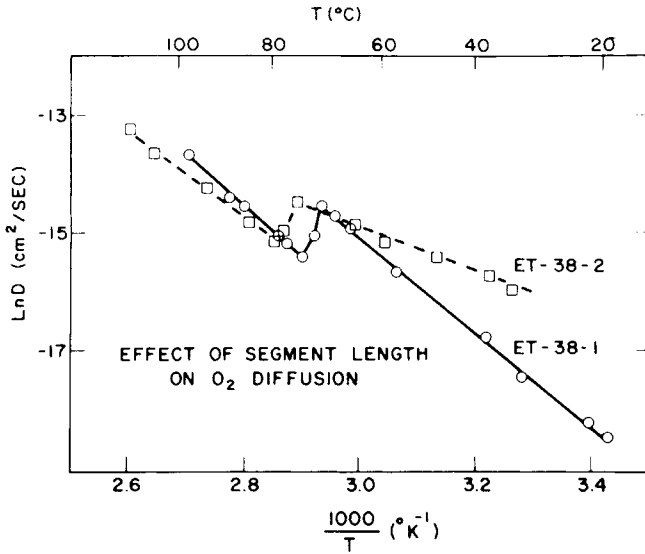
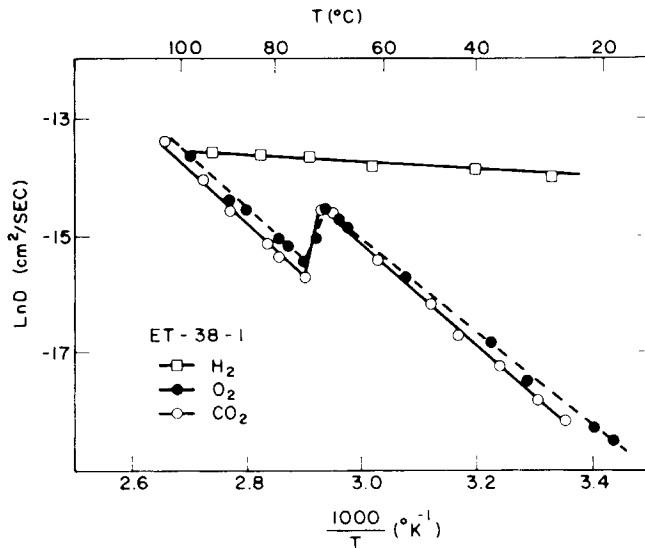Fig. 4. Arrhenius plot for oxygen diffusion through ET-38-1 -O- and ET-38-2 -□-.

Fig. 5. Arrhenius plot for diffusion through ET-38-1 -□- H_2, -●- O_2, and -O- CO_2.

acetate) system, the diffusion coefficient increases by a factor of 10 when the temperature is raised from 17 deg below the polymer's T_g to 17 deg above the T_g.[6] This suggests that the magnitude of the hard domain diffusion coefficient (D_h) is low compared to the soft domain (D_s).

The results of a study concerning the diffusion of simple gases through styrene butadiene styrene (SBS) block copolymers indicated that, indeed, diffusion occurred primarily through the soft butadiene segments at temperatures well below the glass transition temperature of polystyrene.[32] Thus, it does not seem unreasonable to suppose that, at temperatures below the T_g of the hard domain, diffusion occurs primarily through the polyether or polyester segments of the block polyurethanes.
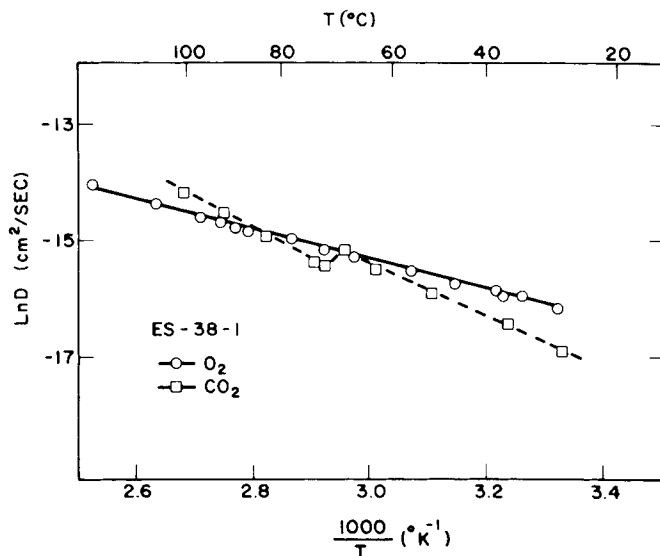
Fig. 6. Arrhenius plot for diffusion through ES-38-1 -o- O_2 and -□- CO_2.

TABLE III
Diffusion Coefficients

Membrane	Penetrant	Diffusivity $(10^7 \text{ cm}^2/\text{sec})$
ET-38-1	O_2	0.24
ET-31-1	O_2	0.96
ET-28-1	O_2	1.22
ET-38-2	O_2	1.06
ES-38-1	O_2	0.96
ET-38-1	H_2	7.53
ET-38-1	CO_2	0.19
ES-38-1	CO_2	0.59

Figure 7 is a plot of the diffusion coefficient of O_2 through ET-38-1, ET-31-1, and ET-28-1 vs percent MDI at 30°C. It may be seen that there is a linear relationship between D and the MDI content. Extrapolating this line to an MDI wt % of zero provides an estimate of what the soft segment diffusivity would be in the absence of hard domains at 30°C. This estimate would not be very meaningful if the ratio D_h/D_s was not approximately zero. It is possible to make similar plots at other temperatures. Table IV lists the extrapolated diffusivity of pure soft segments at several temperatures. It is also possible to construct an Arrhenius plot from the data listed in Table IV. The value of the preexponential is 3.1×10^{-5}/sec and the activation energy is 2.7 kcal/mole.

The activation energies and preexponential factors for the various gas-membrane pairs are listed in Table V. When two lines are required to represent the data, one is designated as occurring in the high-temperature range while the other occurs in the low-temperature range. The following trends may be seen in the low-temperature range: (1) increasing the aromatic content produces an increase in the activation energy and the preexponential factor (Fig. 3); (2) increasing the soft segment length causes the activation energy and preexponential factor to
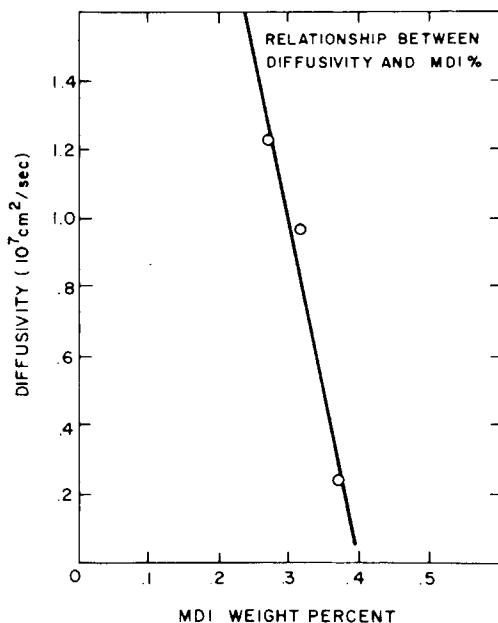
Fig. 7. Plot of O_2 diffusivity vs MDI content at 30°C for ET-28-1, ET-31-1, and ET-38-1.

TABLE IV
Extrapolated Diffusivities of PTMEG in the Absence of MDI

Temperature (°C)	D (10^7 cm²/sec)
20	2.99
30	3.89
40	4.01
50	4.58

TABLE V
Summary of the Arrhenius Parameters for the Polyurethanes

Material	Penetrant	Low-temperature range E_D (kcal/mole)	D_0	High-temperature range E_D (kcal/mole)	D_0
ET-38-1	H_2	1.5	9.1×10^{-6}	—	—
ET-38-1	CO_2	17.4	6.9×10^4	18.8	1.2×10^5
ET-38-1	O_2	15.8	6.1×10^3	17.7	3.2×10^4
ET-31-1	O_2	7.6	2.9×10^{-2}	10.8	2.3
ET-28-1	O_2	5.4	9.6×10^{-4}	7.8	3×10^{-2}
ET-38-2	O_2	8.6	1.7×10^{-1}	14.0	1.4×10^2
ES-38-1	O_2	5.0	3.9×10^{-4}	—	—
ES-38-1	CO_2	8.5	8.05×10^{-2}	10.5	1.06

decrease (Fig. 4); and (3) increasing the penetrant size results in an increase in the activation energy and the preexponential factor (Figs. 5 and 6).

The use of a polyester, rather than a polyether soft segment, causes the activation energy and preexponential factor to decrease.

The fact that an increase in the aromatic content produces an increase in the activation energy suggests that the hard domains are acting as crosslinks and restricting soft segment mobility. The activation energy must increase in order

to overcome these mobility restrictions. This conclusion is not surprising since a large body of experimental evidence exists to support the notion that the hard domains do, indeed, restrain the soft chains. It is interesting to note however, that the mobility restrictions extend to the level at which a diffusing O_2 molecule, 2.98 Å in diameter, "notices" the restrictions.

The polyurethane system can be compared with three other systems: semicrystalline polymers; polymers with reinforcing filler; and chemically crosslinked polymers. Michaels and Bixler observed that the diffusivity decreased as the amorphous content decreased in semicrystalline polyethylene.[33] However, until the crystallites became very large, the activation energy for diffusion did not change. Thus, the crystallites did not act to reduce chain mobility but served to create a more tortuous route for the diffusing molecules. Similar results have been obtained by Van Amerongen for natural rubber filled with a reinforcing agent.[34] The situation is quite different for the case of chemically cross-linked polymers. Generally, as the degree of crosslinking increases, the activation energy for diffusion increases. The crosslinks then, serve to restrict chain mobility. It seems that the capability of the hard domain to diminish chain mobility is comparable to that of a chemical crosslink. This is true despite the fact that the hard domains are physically rather than chemically crosslinked.

The effect of increasing the soft segment is to decrease the activation energy. This is consistent with previous experimental work and indicates that increased soft segment length leads to a lower T_g.[26]

The type of soft segment has a dramatic effect upon the magnitude of the activation energy. The activation energy for the O_2-ET-38-1 pair is nearly three times that of the O_2-ES-38-1 pair. This indicates that the hard domains capacity to restrict soft chain motion is much less in the polyester urethanes, and supports Clough and Schneider's conclusion that the size of the domains is smaller and the degree of phase separation is less in the polyester urethanes.[24,25] Finally, it can be seen that increasing the diameter of the penetrant molecule serves to increase the activation energy.

By referring to Table V, it may be seen that as the aromatic content is increased and with it the mobility restrictions upon the soft segments, the value of the preexponential increases. This may be explained by referring to the Eyring rate theory in which the preexponential is expressed as

$$D_0 = (e\lambda^2 kT/h) \exp(\Delta S^*/R) \tag{6}$$

where λ is the jump length and ΔS^* is the entropy of activation.[35] The entropy of a material whose mobility is restricted to a lesser degree is likely to be greater than a material which has large mobility restrictions. Thus, the entropy change ΔS^* which accompanies the formation of the transition state is likely to be greater for the polymer with the greater mobility restrictions. This phenomenon has also been observed in polymer systems with chemical cross links.[36]

It can be seen from Figures 3–6 that some of the Arrhenius plots are characterized by a narrow temperature range through which the diffusivity decreases with increasing temperature. Above that range, $\ln D$ again increases as a linear function of $1/T$. The slope of the line in the higher-temperature range is greater than the slope of the low-temperature line. Thus, the activation energy has increased through this transition. Table VI lists some characteristics of this discontinuity.

It is readily apparent that the aromatic content has an effect upon the dis-

TABLE VI
Summary of the Discontinuity Characteristics

Material	Gas	Temperature range of discontinuity	Discontinuity size (logarithmic units)
ET-38-1	H_2	—	—
ET-38-1	O_2	68–74	0.88
ET-31-1	O_2	66.5–68	0.36
ET-28-1	O_2	64.5–66	0.19
ET-38-2	O_2	74–78	0.65
ES-38-1	O_2	—	—
ES-38-1	CO_2	67–69	0.31
ET-38-1	CO_2	68–72	1.1

continuity (Fig. 3). Both the magnitude of the transition and the temperature at which it occurs increases with increasing aromatic content. The size of the penetrant molecule is clearly important. For example, the Arrhenius plots of the H_2-ET-38-1 in Figure 5 is just a single line in contrast to the O_2-ET-38-1 and CO_2-ET-38-1 which have discontinuities. Likewise, Figure 6 shows the Arrhenius plot of the O_2-ES-38-1 consisting of one line while the CO_2-ES-38-1 pair shows the transition. It should be pointed out, however, that the size of the penetrant does not seem to affect the temperature at which the phenomenon occurs. The discontinuity for both O_2-ET-38-1 and CO_2-ET-38-1 occur at approximately the same temperature (about 70°C). Increasing the length of the soft segments seems to slightly increase the temperature at which the discontinuity occurs (Fig. 4). Finally, the type of soft segment plays an important role. The O_2-ES-38-1 pair does not show the transition while the O_2-ET-38-1 pair does. The Arrhenius plot of the CO_2-ES-38-1 pair, however, does show the transition. Thus, it seems that the penetrant molecule must be greater than a critical size if the discontinuity is to be seen. This critical size is greater in ES-38-1 than in ET-38-1.

The origin of this phenomenon is not known. Odani et al. obtained similar results with SBS block copolymer.[32] They found that as the temperature was raised above 85°C (approximately the T_g of the polystyrene segments) there were marked deviations from the Arrhenius temperature dependence determined at temperatures below 85°C. Indeed, the diffusivities tended to decrease above this temperature. These deviations which were more marked as the size of the penetrant was increased, were not explained. This discontinuity, which is also seen in the current data, may be associated with the multiphase character of the block polymers and may, in fact, be the observation of the glass transition of the hard domains. In the polyurethanes as the temperature is increased, the hard domains begin to soften. Curves obtained using DSC indicate that, depending upon annealing history, there is a loss of short-range order in the hard domains at 70°C. This suggests that there is an increased capability for the chains in the hard domains to move. Finally, at the T_g of the hard segments, chain mobility is increased to such a level in the hard domains that hydrogen bonds begin an accelerated rate of dissociation.[27] Similar softening takes place within the polystyrene regions of the SBS copolymer. Presumably, this increase in hard chain mobility is accompanied by an increase in hard domain diffusivity. Perhaps at a temperature near the T_g of the hard domains the magnitude of the hard domain diffusivity increases to a level such that it becomes a significant diffusion

pathway. Prior to this temperature level, the observed diffusivity was essentially that of the soft domains. At this temperature, however, the observed diffusivity contains contributions from both phases. The activation energy increases because the diffusion process becomes more difficult as gas molecules begin diffusing through the hard domains. Thus, the discontinuity is the zone during which significant quantities of gas molecules begin to cross the hard domains.

The temperature range over which the discontinuity phenomenon occurs tends to support the hypothesis that the softening of the hard domains is involved in the phenomenon. The T_g of the hard domains found by Seymour and Cooper in their study of the thermal dependence of hydrogen-bond disruption is very near this temperature range.[27] They also showed that the temperature of the hard domain glass transition increases with longer hard segment block lengths. In the diffusion data also, the temperature range of the discontinuity increases with hard block length.

CONCLUSIONS

A mass spectrometric method was used to study diffusion of gases through polyurethane block polymers. A series of segmented polyurethanes were studied with varying hard segment weight percent, segment length, and type of soft segment. In addition the penetrant size of the diffusing species and the temperature at which the diffusion experiments were carried out were varied. The experimental results revealed that increasing the hard segment weight percent caused the diffusion coefficient to decrease and brought about an increase in the activation energy and preexponential factor of diffusion. In contrast, increasing the soft segment length caused an increase in the diffusivity and a decrease in the Arrhenius parameters. Studying a polyurethane with a polyester rather than a polyether soft segment showed an increase in the diffusivity and a decrease in the activation energy and preexponential factor. Increasing the diameter of the penetrant caused a decrease in the diffusion coefficient and an increase in the Arrhenius parameters. As the penetrant size was increased, a discontinuity was introduced into the Arrhenius plots for both the polyether and polyester urethanes.

It may be concluded that at temperatures well below the T_g of the hard segments the hard domains serve to restrict the mobility of the soft chain segments. This mobility restriction is at a level such that the diffusion of O_2 or CO_2 molecules is affected. At temperatures near the T_g of the hard segments, the diffusion process undergoes a modification. This manifests itself as a discontinuity in some of the Arrhenius plots. It was suggested that as the temperature is raised to near the T_g, the hard domains begin to participate to a significant extent in the diffusion process. It was also observed that the critical size of the penetrant required to see the discontinuity in an Arrhenius plot is greater in polyester urethanes than in polyether urethanes. This tends to support the conclusion that the degree of phase separation is less in polyester urethanes.

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