# Effect of tensile deformations on gas transport in glassy polymer films

**Thor L. Smith and Randall E. Adam***
*IBM Research Laboratory, San Jose, California* 95193, *USA*
(*Received* 1 *May* 1980; *revised* 23 *June* 1980)

An exploratory study has been undertaken to determine the effect of simple tensile deformations, applied stepwise, on the permeability and diffusion coefficients ($P$ and $D$) of gases in glassy polymers. For nitrogen in a polycarbonate film at 73°C, it was found that $(1/P)\mathrm{d}P/\mathrm{d}\epsilon \simeq 13$ and $(1/D)\mathrm{d}D/\mathrm{d}\epsilon \simeq 5$ to 8, where $\epsilon$ is the strain. Also, $P$ and $D$ were found to decrease with time at constant strain and to depend somewhat on strain and thermal histories. A calculation of $(1/D)\mathrm{d}D/\mathrm{d}\epsilon$, based primarily on considerations of free volume and its strain dependence, gives 11.8 or 8.5, depending on the assumptions made. Progressive stepwise application of strain to a polyimide (Kapton) film at 72° and 125°C caused $P$ and $D$ for carbon dioxide to increase. But above 2% strain at 125°C, they decreased until at 6% strain they became smaller than those for the undeformed specimen, a reflection of a strain-induced relaxation process.

## INTRODUCTION

The transport of gases in glassy polymers has been studied extensively[1–4], but little is known about its dependence on changes in volume effected by volume recovery[5] (densification), hydrostatic pressure, or tensile stress. Chen[6] has shown that the diffusion coefficients of hydrocarbon gases in amorphous poly(ethylene terephthalate) and polycarbonate films decrease progressively with annealing time at about 25°C below their glass temperatures. The diffusion coefficient should therefore increase when a specimen is dilated by a tensile stress, as observed by Rosen[7]. He showed that the flux of nitrogen and helium through a biaxially-oriented polystyrene film was increased markedly by a biaxial tensile deformation, although crazing undoubtedly caused part of the increase[8].

Although no other studies of the strain dependence of gas transport in glassy polymers have been reported, Yasuda *et al.*[9] found that the permeability coefficients of nitrogen and helium in lightly-vulcanized natural rubber are unchanged when a specimen is stretched biaxially at strains up to 24% ($\varepsilon_1 \simeq \varepsilon_2$). This finding, which is similar to that reported for hydrocarbon vapours[10], was anticipated because the volume of rubber is affected insignificantly by tensile deformations, unless crystallization occurs. In contrast, the permeability coefficients of various gases in polyethylene and polypropylene films were found to increase substantially when the films were stretched biaxially.

Subsequently, Yasuda and Peterlin[11] studied the effect of simple tensile strains on the permeability and diffusion coefficients ($P$ and $D$, respectively) of carbon dioxide in polyethylene. The observed increase in $P$ and $D$ followed by a decrease with increasing strain was attributed[12] to strain-induced dilation of the specimen and to changes in crystal morphology.

The sorption and transport of gases in glassy polymers, even when undeformed, are commonly complex processes that seemingly are in accord with the dual-sorption and dual-mobility models which have been succinctly reviewed by Paul[4] in the light of recent experimental data.

An investigation is currently being undertaken to determine the effect of simple tensile strains, and strain history more generally, on the transport of gases in glassy polymers. Results from exploratory measurements are presented herein, and those from a systematic study, primarily of gas transport in biaxially-oriented polystyrene, will be presented later[13]. These studies should provide additional information on the mechanism of gas transport and, in turn, on the structure of glassy polymers and its modification by stress.

## EXPERIMENTAL

### *Materials*

The films studied were 1 mil* polyimide (Kapton, type H) produced by E. I. du Pont de Nemours and Co. and 3 mil polycarbonate obtained from the General Electric Co. and from Rodyne Industries Inc., Mt. Vernon, NY, designated herein as Lexan and Rodyne, respectively.

The purity of the carbon dioxide and nitrogen used in the experiments was at least 99.5% and that of the helium was 99.999% or better. To remove any oil or water, each gas was passed over a molecular sieve in a drying tube installed on the line leading to the permeation apparatus. The thermal conductivity detector in the apparatus was calibrated with UHP (ultra high purity) helium containing 0.1006% UHP nitrogen. This mixture was obtained from the Matheson Co.

### *Apparatus*

The permeability and diffusion coefficients for a gas were derived from the steady-state and time-dependent

---

* Present address: Central Research, 3M Company, St. Paul, Minnesota, USA

* 1 mil = 25.4 $\mu$m

0032 3861/81/030299 06$02.00

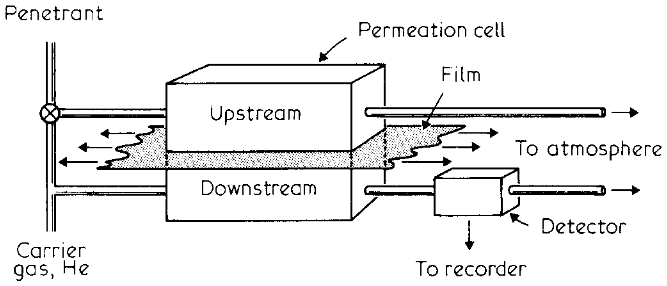

*Figure 1* Sketch of apparatus used to measure the permeation rate of gases through polymer films

permeation rates measured with a Polymer Permeation Analyzer obtained from the Dohrmann Division of Envirotech Corp., Santa Clara, CA. This apparatus is a version of that developed by Pasternak *et al.*[14] and is similar in principle to that described by Ziegal *et al.*[15] and Caskey[16].

As indicated schematically in *Figure 1*, a carrier gas (helium for the present study) passes through the downstream chamber of the permeation cell and then through one side of a thermal conductivity detector. Though not shown, helium also passes through the other side of the detector. Initially, helium also passes through the upstream chamber of the cell. To begin an experiment, the helium stream in the upstream chamber is replaced by a stream of the penetrant gas. As the gas permeates the film, it is entrained by the carrier gas flowing to the detector. The resulting signal $S(t)$, which is monitored by a strip-chart recorder and is proportional to the flux of the penetrant, gradually increases to a steady-state value, $S_\infty$. Because the flow rate of the carrier gas is much greater than the penetrant flux, the partial pressure of the penetrant in the carrier gas is low.

The film is held in the cell by an O-ring, outside of which is a groove purged by helium to prevent air from entering the cell. The downstream chamber is mounted on a supported metal plate. The upstream chamber is attached to a rod spring assembly which enables it to be raised and lowered quickly by turning a cam, a convenience for making measurements on a stretched film. To do this, one end of a film strip about 5 x 25 cm is clamped at one end of a metal frame; the other end is passed through a slotted rod which can be turned by a worm gear. The frame is mounted such that the film passes between the two chambers of the permeation cell. An air chamber whose temperature can be controlled up to 150°C surrounds the holder and cell. After a permeation measurement has been made, the cell is opened, the film is stretched a known amount by turning the worm gear, and the cell is then closed. These operations can be made without opening the air chamber and thus without disturbing the temperature appreciably.

### *Calculations*

The signal $S(t)$ recorded during an experiment gives an asymmetrical sigmoidal curve, as illustrated elsewhere[14,15], and becomes $S_\infty$ at steady-state. The diffusion coefficient derived from such a curve is probably an effective value because this coefficient for a gas in a glassy polymer depends in general on its pressure[4]. The permeability coefficient, although it may also depend on pressure, refers to the rate of transport of the penetrant under specified conditions.

The permeability coefficient equals the flux divided by $p/L$, where $p$ is the upstream pressure of the penetrant (1 atm for the present experiments) and $L$ is the film thickness. Hence:

$$P = fkbS_\infty / A(p/L) \tag{1}$$

where $f$ is the volumetric flow rate of the carrier gas, $k$ is the response factor of the detector to the penetrant, $b$ is the detector attenuation, and $A$ is the area of the specimen.

The effective diffusion coefficient is here evaluated by the method of Pasternak *et al.*[14] which is based on the equation:

$$N(t)/N_{ss} = (4/\sqrt{\pi})(L^2/4Dt)^{1/2}\, exp(-L^2/4Dt) \tag{2}$$

where $N(t)$ and $N_{ss}$ are the time-dependent and steady-state fluxes, respectively. Equation (2) is stated[14] to be the first-order approximation to the exact equation and to be valid for $N(t)/N_{ss} < 0.97$.

To evaluate $D$, values of $S(t)/S_\infty$ [$= N(t)/N_{ss}$] are obtained from the recorder trace. The corresponding values of $4Dt/L^2$ are derived from equation (2) and plotted against time. Provided equation (2) represents $S(t)/S_\infty$, the plot yields a straight line whose slope is given by :

$$\text{Slope} = 4D/L^2 \tag{3}$$

Because $D$ is proportional to the slope, the point of zero time on the $S(t)$ curve need not be known. Zero time is when the penetrant contacts the film and not when the recorder trace leaves the baseline.

*Figure 2* shows illustrative plots. The scales on the right- and left-hand ordinates represent, respectively, $S(t)/S_\infty$ and the corresponding values of $4Dt/L^2$ given by equation (2). When the flow rate of the carrier gas was 0.127 $cm^3\ s^{-1}$, the data define the line on the right whose slope gives $6.69 \times 10^{-7}$ $cm^2\ s^{-1}$ for the diffusion coef-

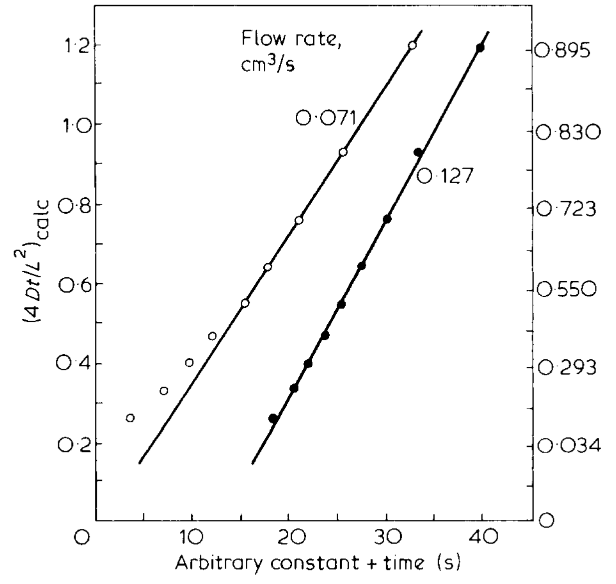

*Figure 2* Plots prepared to evaluate the diffusion coefficient of nitrogen in a 3 mil polycarbonate film at 105°C and also to determine whether the reduced flux $S(t)/S_\infty$ conforms to equation (2). Open and shaded circles represent data obtained when the flow rate of the carrier gas (helium) was 0.071 and 0.127 $cm^3$ (s.t.p.)/s respectively

ficient. But when the flow rate was 0.071 cm$^3$ s$^{-1}$, the four lowest points lie above the left straight line whose slope gives a lower diffusion coefficient, i.e. 5.55 × 10$^{-7}$ cm$^2$ s$^{-1}$. Thus, if the flow rate of the carrier gas is too low, equation (2) does not represent $S(t)/S_{\infty}$ over an extended range and a low value of $D$ is obtained. This behaviour presumably results, at least partly, because the flux increases significantly during the time required for a small volume of the carrier gas to pass through the downstream chamber of the permeation cell and thus $S(t)$, observed subsequently, is proportional to some time-average flux and not the instantaneous value. In the present study, the flow rates of the carrier gas employed were sufficiently large so that the $S(t)$ data gave plots like that shown on the right in *Figure 2*.

When an isotropic specimen is subjected to a strain $\varepsilon$ in simple tension, the strain in the thickness direction is given by $\varepsilon_3 = -\nu\varepsilon$, provided $\varepsilon$ is sufficiently small, where $\nu$ is Poisson's ratio. This relation and equations (1) and (3) lead to:

$$P = P'(1 - \nu\varepsilon) \qquad (4)$$

$$D = D'(1 - 2\nu\varepsilon) \qquad (5)$$

where $P'$ and $D'$ are based on the thickness of the specimen at zero strain.

In the present study, $P'$ and $D'$ were converted into $P$ and $D$ by equating $\nu$ to 0.50 which is approximately valid only when $\varepsilon$ exceeds the yield strain and the deformation is small and homogeneous. At small strains, the deformation of a glassy polymer is nearly elastic, and $\nu$ typically is between 0.3 and 0.4. However, under such conditions, $P/P'$ and $D/D'$ are rather insensitive to changes in $\nu$. For example, when $\varepsilon = 0.02$, $D/D'$ is 0.986 and 0.980 when $\nu$ equals 0.35 and 0.50, respectively.

## RESULTS AND DISCUSSION

### *Polycarbonate films*

Early experimental results are displayed in *Figure 3* which shows the strain dependence of the permeability coefficient of nitrogen in a 3 mil polycarbonate (Lexan) film at 128°C. After stretching the specimen stepwise to about 2% (full circles) and then allowing it to recover under zero stress, $P$ was somewhat less than its initial value (*Figure 3*). This finding is probably valid in view of the data in *Figure 4*, discussed subsequently. The open circles in *Figure 3* represent data obtained during the second stepwise stretching of the specimen. (The time between each measurement was ordinarily in excess of 30 minutes.) The minimum in the curve at about 3% strain probably resulted because the specimen remained stretched overnight, and $P$ decreased during that period.

The slope of the line that represents the data obtained during the first stretching of the specimen corresponds to about 7.8% increase in $P$ per unit strain expressed as percentage strain. Alternatively, $(1/P)\mathrm{d}P/\mathrm{d}\varepsilon = \mathrm{d}\ln P/\mathrm{d}\varepsilon = 7.8$ where $\varepsilon$ is the strain and not the percentage strain. Throughout this paper, whenever $(1/P)\mathrm{d}P/\mathrm{d}\varepsilon$ and $(1/D)\mathrm{d}D/\mathrm{d}\varepsilon$ are given as a percentage, then $\varepsilon$ is expressed as percentage strain.

At large strains during the second stretching of the specimen, $(1/P)\mathrm{d}P/\mathrm{d}\varepsilon$ is about 14.5%. The total increase in $P$ in going from zero to 4.8% strain is about 65%, i.e. $(\Delta P/P_0) \times 100 = 65$ where $P_0$ is the value at zero strain. However, the increase in $P$ at strains greater than 3% is ascribed to crazing of the specimen.

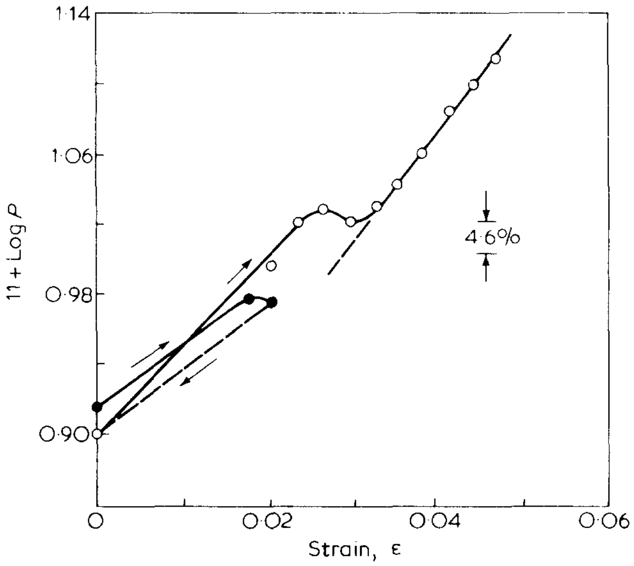

*Figure 3* Strain dependence of the permeability coefficient of nitrogen in a 3 mil polycarbonate film at 128°C. Data from first and second stretching of specimen stepwise shown by shaded and open circles, respectively. Decrease in $P$ at about 2.5% strain presumably resulted because this strain was maintained overnight. Increase in $P$ at larger strains resulted from crazing of specimen. Units of $P$ are: cm$^3$ (s.t.p.) cm/cm$^2$ · s · cmHg

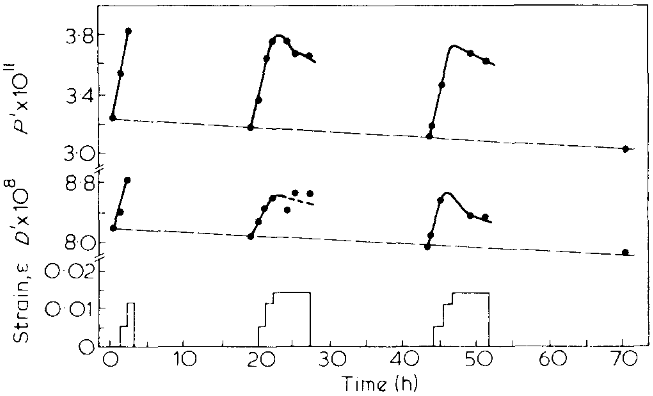

*Figure 4* Strain and time dependence of the permeability and diffusion coefficients of nitrogen in a 3 mil polycarbonate film at 73°C

A 3 mil polycarbonate film (Lexan, as-received) was subjected at 73°C to the strain history shown at the bottom of *Figure 4*, and both $P$ and $D$ for nitrogen were determined at each strain. The resulting data show that both $P$ and $D$ increase with strain but they decrease with time at a constant strain of 1.5%. A finding of special significance, shown by the dashed straight lines and discussed below, is the progressive decrease of $P$ and $D$ for nitrogen in the unstressed specimen after each deformation cycle.

Another specimen was heated for 2.5 h at 150°C, which is approximately the glass transition temperature, and then quenched in ice water. Measurements similar to those described above were begun on the quenched specimen whose free volume undoubtedly exceeded that for the as-received specimen. However, during the second deformation cycle, crazes developed and gave a large

*Table 1* Results from measurements of the transport of nitrogen in as-received (A–R), quenched (Q), and annealed (A) polycarbonate films at 73° and 50°C

| | 73°C | | 50°C | |
|---|---|---|---|---|
| Quantity | A–R | Q | A | Q |
| $(P \times 10^{11})_{\epsilon=0}$ | 3.24 | 3.38 | 2.00 | 2.29 |
| $(D \times 10^{8})_{\epsilon=0}$ | 8.2 | 8.5 | 3.26 | 3.70 |
| $(1/P)(\mathrm{d}P/\mathrm{d}\epsilon)$ | 13 | 9 | – | – |
| $(1/D)(\mathrm{d}D/\mathrm{d}\epsilon)$ | 5, 8[a] | 4(?) | – | – |
| $(1/P_0)(\mathrm{d}P/\mathrm{d}t)$[b] | $-7.7 \times 10^{-4}$ | $-9.9 \times 10^{-4}$ | – | – |
| $(1/D_0)(\mathrm{d}D/\mathrm{d}t)$[b] | $-6.0 \times 10^{-4}$ | $-10.3 \times 10^{-4}$ | – | – |

[a] At 63°C

[b] Evaluated at zero strain; $t$ is expressed in hours; $P_0$ and $D_0$ are the permeability and diffusion coefficients, respectively, at zero time

value for $P$. (The data obtained on the quenched film are now shown here.)

Two specimens of 3 mil polycarbonate (Rodyne) film were heated for 1 h at 160°C. One specimen was then quenched in ice–water, and the other (termed annealed) was cooled at 0.25°C min$^{-1}$. As indicated by the data in *Table 1*, $P$ and $D$ for nitrogen in the quenched film at 50°C are 14% larger than those in the annealed film, a consequence of the difference in free volume. For a similar reason, $P$ and $D$ for nitrogen in the as-received film at 73°C are smaller ($\sim$4%) than those for the quenched film.

*Table 1* also shows that $(1/P)\mathrm{d}P/\mathrm{d}\varepsilon$ and $(1/D)\mathrm{d}D/\mathrm{d}\varepsilon$, obtained from the first stretching of the films at 73°C, are about 13% and 5%, respectively, for the as-received film but are about 9% and 4%, respectively, for the quenched film. Data obtained at 63°C indicate that $(1/D)\mathrm{d}D/\mathrm{d}\varepsilon \simeq 8$. The results are not sufficiently reliable, however, to conclude that $(1/D)\mathrm{d}D/\mathrm{d}\varepsilon$ actually increases with a reduction in the temperature from 73° to 63°C.

Although certain quantities, especially $(1/D)\mathrm{d}D/\mathrm{d}\varepsilon$, are probably not highly precise, the data clearly show that the strain dependence of $P$ and $D$ for the as-received film is greater than for the quenched film. As discussed subsequently, $(1/D)\mathrm{d}D/\mathrm{d}\varepsilon$ is proportional to $(1-2\nu)/f^2$, where $f$ is the fractional free volume. Because both $\nu$ and $f$ are larger for the quenched than for the annealed specimen, it follows that $(1/D)\mathrm{d}D/\mathrm{d}\varepsilon$ and undoubtedly $(1/P)\mathrm{d}P/\mathrm{d}\varepsilon$ also should be smallest for the quenched specimen, as observed.

Because $P$ increases with strain more rapidly than $D$, the solubility of nitrogen in the polycarbonate film probably increases with the strain even though $P/D$ for glassy polymers often cannot be equated to the Henry's law solubility coefficient[4].

The broken straight lines in *Figure 4* show that $P$ and $D$ for nitrogen in the as-received film at zero strain decrease with the number of deformation cycles. The slopes of these lines and those (not shown) for the annealed film give the values of $(1/P_0)\mathrm{d}P/\mathrm{d}t$ and $(1/D_0)\mathrm{d}D/\mathrm{d}t$ presented in *Table 1*, where $P_0$ and $D_0$ refer to the film at zero time. Although these quantities for each film are equal within the probable experimental uncertainty, the absolute values for the quenched film clearly exceed those for the as-received film. This behaviour is ascribed to the greater tendency of the quenched film to contract volumetrically.

Probably, $(1/P_0)\mathrm{d}P/\mathrm{d}t$ and $(1/D_0)\mathrm{d}D/\mathrm{d}t$ exceed those for a specimen not subjected to deformation cycles. Chen[6] measured the time dependence of $D$ for methane in an unstrained polycarbonate film at 120°C. His data between 10 and 125 h show that $(1/D_0)\mathrm{d}D/\mathrm{d}t$ at 120°C is essentially the same as that for our as-received film at 73°C (*Table 1*). Therefore, it is proposed that the periodic application of tensile strains (*Figure 4*) accelerated the densification process, as reported by Sternstein and coworkers[17,18] from studies of the viscoelastic properties of glassy polymers. Because both tensile and compressive strains were found to accelerate densification, a process termed mechanically enhanced aging[18,19], it was concluded[18] that the acceleration is caused by the distortional (deviatoric) strain energy and not directly by the dilation effected by a tensile deformation.

### *Polyimide film*

A few measurements were made of the strain dependence of $P$ and $D$ for carbon dioxide in a 1 mil polyimide (Kapton) film at several temperatures. The results along with those obtained subsequently[20] indicate that the behaviour is complex and cannot be explained readily.

*Figure 5* shows that $P$ and $D$ at 72°C increase with the strain, applied stepwise, although the rate of increase is rather low, the total increase being about 12%. At 125°C, $P$ and $D$ first increase with the strain; they then decrease and eventually become less than the initial values. Similar behaviour was found at 150°C (data not presented here). These observations indicate that a relaxation process at 125° and 150°C overshadows the expected increase in $P$ and $D$ with strain and causes $P$ and $D$ to decrease at strains greater than 2 or 3%. (The time between each change in the strain was no less than 30 to 60 min.) Subsequent measurements[20] at 150°C showed that $P$ decreases about 4% per decade of time at a constant strain of 6% and after 18 h becomes 5% less than found initially for the unstrained specimen.

While the time-dependent decrease of the permeability of a polycarbonate film at a constant strain (*Figure 4*) can be ascribed to a densification of the specimen, this process undoubtedly does not account fully for the behaviour of

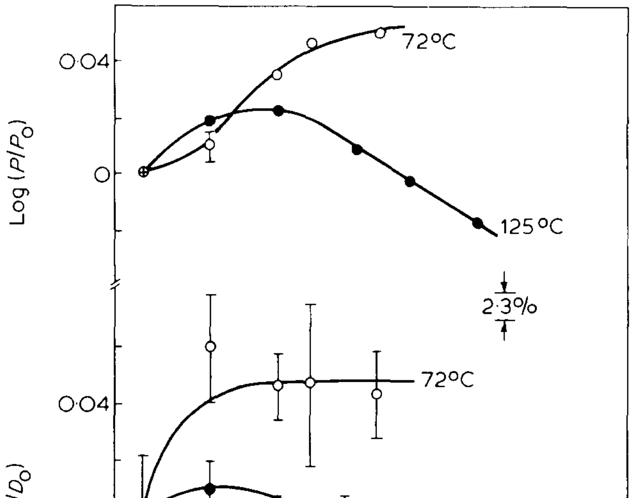

*Figure 5* Strain dependence of the permeability and diffusion coefficients of carbon dioxide in a 1 mil polyimide (Kapton) film at 72° and 125°C

the polyimide film whose properties are most unusual. Its glass transition temperature[21], if one exists in fact, is greater than 500°C. Nevertheless, its stress–strain curves show no well-defined yield point, and the elongation-at-break is 55% at 25°C and 75% at 150°C. Possibly the unusual dependence of $P$ and $D$ on strain and time results from some type of change in microstructure.

## THEORETICAL CONSIDERATIONS OF THE STRAIN DEPENDENCE OF THE DIFFUSION COEFFICIENT

Qualitatively, the enhancement of $P$ and $D$ by strain undoubtedly results from the accompanying dilation of a specimen. However, because the nature of the modified diffusion process is not known precisely, a quantitative explanation cannot be given. As mentioned above, the transport of a gas through an undeformed glassy polymer is commonly a complex process, not entirely understood[4]. Overlooking such complexities and the role played by relaxation processes, we shall consider certain factors that likely are responsible for the strain dependence of $D$.

As discussed by Turnbull and Cohen[22], the excess volume $(v-v_0)$ of an undeformed specimen is given by:

$$v-v_0=v_f+\Delta v_c \tag{6}$$

where $v$ is the specific volume, $v_0$ is the volume occupied by the molecules (van der Waals volume), $v_f$ is the free volume, and $\Delta v_c$ is that portion of the excess volume that requires energy for redistribution and which results from the 'anharmonicity of the vibrational part of the motion' of atoms or segments in their cages[22]. Stated otherwise, $v_f/v$ $(=f)$ is the fractional free volume defined as that portion of $(v-v_0)/v$ which can be redistributed without an increase in energy.

Analysis of the temperature dependence of the viscosity or viscoelastic properties of various polymers above the glass transition temperature $T_g$ in terms of the Williams–Landel–Ferry (WLF) equation indicates[23] that $f_g/B_v$ is about $0.025\pm0.005$, where $f_g$ is the fractional free volume at $T_g$ and $B_v$ is a constant, usually equated to unity[23]. With a temperature decrease below $T_g$, the volume contraction affects $\Delta v_c$ primarily and $v_f/v$ only slightly, if at all[22,23].

For a penetrant whose size exceeds a critical value, its diffusion coefficient at low concentrations in a polymer above $T_g$ is approximately proportional to $\exp(-B/f)$, where $B$ is considered to be a constant for a particular penetrant–polymer pair[24–26]. When this relation is obeyed, the transport rate of a penetrant is affected, or possibly controlled, by the mobility of polymeric segments which depends on free volume, among other things. Also, the apparent activation energy is temperature dependent because $f$ increases linearly with (not proportional to) temperature[27]. At temperatures significantly below $T_g$, the fractional free volume is essentially temperature independent and then diffusion is a thermally-activated process. By combining rate theory and free-volume theory, Macedo and Litovitz[28] obtained:

$$D=D_0\exp[-(B/f+E^*/RT)] \tag{7}$$

where $D_0$ is a weak function of temperature, $E^*$ is an activation energy, and $RT$ is the product of the gas constant and the absolute temperature. (Vrentas and Duda[26,28] have recently discussed this equation.)

Equation 7, which has not been widely used, accounts semiquantitatively for the effect of free volume and thermal activation on diffusion. It accounts qualitatively for the apparent activation energy being temperature dependent above $T_g$ and also for the marked increase in the apparent activation energy as the temperature is increased from below to above $T_g$, which is observed provided the penetrant molecule is not unduly small[29].

Assume now that $f$ is essentially independent of temperature and time below $T_g$ and that $B$ and $D_0\times\exp(-E^*/RT)$ are independent of strain. Hence, differentiation of equation (7) with respect to strain at constant temperature gives:

$$(1/D)\mathrm{d}D/\mathrm{d}\varepsilon=(B/f^2)\mathrm{d}f/\mathrm{d}\varepsilon\simeq(B/f_0^2)\mathrm{d}f/\mathrm{d}\varepsilon \tag{8}$$

where $f_0$ $(\simeq f)$ is the fractional free volume at zero strain. To apply this equation, it is necessary to evaluate $B$, $f_0$, and the strain dependence of $f$.

The strain dependence of $f$ can be evaluated by first noting that, according to definition, the isothermal compressibilities of a specimen and of its free volume are given by $\beta=-(1/v)\mathrm{d}v/\mathrm{d}p$ and $\beta_f=-(1/v)\mathrm{d}v_f/\mathrm{d}p$, respectively. When a specimen is subjected to simple tension, the fractional increase in volume is given by $(1/v)\mathrm{d}v/\mathrm{d}\varepsilon=1-2\nu$. (This relation, which is strictly applicable only when the strains are infinitesimal, is from elasticity theory.) From these three relations, the following results:

$$\mathrm{d}f/\mathrm{d}\varepsilon=(\beta_f/\beta-f)(1-2\nu)\simeq(\beta_f/\beta)(1-2\nu) \tag{9}$$

The approximate relation above, which is that given by Ferry and Stratton[23,30], results because $f$ is usually small compared with $\beta_f/\beta$. It now follows from equations (8) and (9) that:

$$(1/D)\mathrm{d}D/\mathrm{d}\varepsilon\simeq(B/f_0^2)(\beta_f/\beta)(1-2\nu) \tag{10}$$

Though the discussion by Turnbull and Cohen[22] of their model implies that $\beta_f\approx0$ at temperatures significantly below $T_g$, the substantial short-range segmental motion in polycarbonate over an extended range below $T_g$[31,32] indicates that $\beta_f$ is undoubtedly finite at the temperatures of interest here. To estimate $\beta_f/\beta$, we first note that $\mathrm{d}T_g/\mathrm{d}p=\beta_f/\alpha_f$, provided the free volume of a polymer at $T_g$ is a constant[23], where $\alpha_f$ is the thermal expansion coefficient of the free volume. Reported values of $\mathrm{d}T_g/\mathrm{d}p$ for polycarbonate are 0.04°C $\mathrm{atm}^{-1}$[31] and 0.044°C $\mathrm{atm}^{-1}$[33]. As an expediency, we now assume that $\alpha_f=\alpha_1-\alpha_g$, where $\alpha_1$ and $\alpha_g$ are the thermal expansion coefficients above and below $T_g$. According to unpublished data reported by O'Reilly[33], $\alpha_f=3.78\times10^{-4}$ °C$^{-1}$ which agrees closely with that from other volumetric expansion data presented graphically[31a] and with $3.9\times10^{-4}$ from data of Hellwege *et al.*, tabulated elsewhere[34]. (Another value[35] of $\alpha_f$ is $2.8\times10^{-4}$ °C$^{-1}$, which probably is in error.) Taking $\mathrm{d}T_g/\mathrm{d}p\simeq0.04$°C $\mathrm{atm}^{-1}$, $\alpha_f=3.8\times10^{-4}$ °C$^{-1}$, and $\beta=3\times10^{-5}$ $\mathrm{atm}^{-1}$[34], which is the compressibility below $T_g$, we obtain $\beta_f/\beta=0.51$.

$D$ for various gases and vapours at low concentration in polycarbonate at 55°C can be represented by $\ln(D/A)=-0.35d^2$, where $d$ is the diameter in Å of the penetrant and A is a constant[6]. A comparison of this relation with equation (7) indicates that $\ln(D/A)=-B/f$, where $A=D_0\exp(-E^*/RT)$. As $d$ for nitrogen[36] is 3.7Å, it follows that $B/f_0=4.79$ at 55°C.

From data presented recently by Chen and Edin[37], it can be deduced that the slope of a plot of $\ln(D/A)$ vs. $d^2$ increases with a decrease in temperature. Also, they represent data at 120°C, which extend to larger values of $d$ than those considered earlier[6], by a line whose slope equals that given above. However, when $d \leqslant 5.24$ Å, the data at 120°C can be represented by a line whose slope would be about $-0.35$ at 55°C. Thus, because the value given above for $B/f_0$ is not highly precise, its slight temperature dependence will be overlooked.

Yee[38] has found that $\nu = 0.43$ for an annealed compression-moulded specimen of polycarbonate at temperatures from 25° to 70°C. Other measurements[39] have given $\nu \simeq 0.40$.

Substitution of $\beta_f/\beta = 0.51$ and $\nu = 0.43$ in equation (10) along with $B/f_0 = 4.79$ and $f_0 \simeq f_g = 0.029$[31b] gives $(1/D)\mathrm{d}D/\mathrm{d}\varepsilon = 11.8$. This calculated value exceeds those measured (*Table 1*), which are about 5 and 8 at 73° and 63°C. The disagreement possibly results from uncertainties in the experimental values and that calculated, the latter being quite sensitive to the selected values of the parameters in equation (10). For example, if $\beta_f/\beta$ in equation (10) is replaced by $(\beta_f/\beta - f_0)$ and $\nu$ is equated to 0.44 instead of 0.43, the calculated value is 9.5 instead of 11.8.

Recently it has been found[13] that $(1/D)\mathrm{d}D/\mathrm{d}\varepsilon = 15$ for carbon dioxide in polycarbonate at 50°C. As $B/f_0 = 0.35d^2$ at 55°C and $d$ for carbon dioxide[36] is 3.9 Å, it follows that $B/f_0 = 5.32$. Substitution of this value in equation (9) and the values given above for the other parameters leads to $(1/D)\mathrm{d}D/\mathrm{d}\varepsilon = 13.1$, in close agreement with the experimental result.

If equation (10) is accepted, though its appropriateness can be questioned, it is by no means clear whether the selected values of $\beta_f/\beta$ and $f_0$ are the proper ones to use, especially at temperatures significantly below $T_g$. As an alternative approach, $f_0$ can be replaced by the fraction of excess volume, $(v - v_0)/v$. This quantity is about 0.11 at $T_g$ for many polymers[40,41]. If $\alpha_g = 3.9 \times 10^{-4}\,{}^{\circ}\mathrm{C}^{-1}$ [34], then $(v - v_0)/v = 0.079$ at 63°C. Substituting this value in place of $f_0$ in equation (10) along with $B/f_0 = 4.79$ and $\nu = 0.43$, as before, and equating $\beta_f$ to $\beta$ gives $(1/D)\mathrm{d}D/\mathrm{d}\varepsilon = 8.5$ for nitrogen at 63°C, in good agreement with the experimental value.

However, this alternative approach for calculating $(1/D)\mathrm{d}D/\mathrm{d}\varepsilon$ gives 10.1 for carbon dioxide in polycarbonate at 50°C, in poor agreement with 15, the experimental value given above. Hence, it is unclear which of the two methods for calculating $(1/D)\mathrm{d}D/\mathrm{d}\varepsilon$ is most reliable.

The present experimental results showing the strain dependence of $P$ and $D$ are not highly precise because, among other things, these quantities decrease with time at constant strain, and this time dependence has been ignored. As several hours are required to measure $D$, for example, at several strains, the derived $(1/D)\mathrm{d}D/\mathrm{d}\varepsilon$ will depend on the total time and will be somewhat less than that given by values of $D$ when each is measured at the same value of time. Obtainment of the latter requires plots of $\log D$ vs. $\log t$ where each plot represents data at a different strain.

Finally, it is of interest to note that when a film is subjected to uniform biaxial tension, $(1/D)\mathrm{d}D/\mathrm{d}\varepsilon$ should be several-fold larger than when the deformation is simple tensile. In uniform biaxial tension, $v^{-1}\mathrm{d}v/\mathrm{d}\varepsilon = 2(1-2\nu)/(1-\nu)$ compared with $(1-2\nu)$ in simple tension. Hence, if $\nu = 0.43$, $(1/D)\mathrm{d}D/\mathrm{d}\varepsilon$ should be 3.5-fold larger in uniform biaxial tension than in simple tension.

## REFERENCES

1 'Diffusion in Polymers', (Eds. Crank and Park), Academic Press, New York, 1968
2 Hopfenberg, H. P. and Stannett, V. in 'The Physics of Glassy Polymers', (Ed. Haward), Wiley, New York, 1973, p 504
3 Bixler, H. J. and Sweeting, O. J. in 'The Science and Technology of Polymer Films', Vol. II, (Ed. Sweeting), Wiley-Interscience, New York, 1971, p 1
4 Paul, D. R. *Ber. Bunsenges. Phys. Chem.* 1979, **83**, 294
5 Kovacs, A. *Adv. Polym. Sci.* 1964, **3**, 394
6 Chen, S. P. *Polym. Preprints* 1974, **15**(1), 77
7 Rosen, B. *J. Polym. Sci.* 1960, **47**, 19
8 Rosen, B. in 'Fracture Processes in Polymeric Solids', (Ed. Rosen), Wiley-Interscience, New York, 1964, p 293
9 Yasuda, H., Stannett, V., Frisch, H. L. and Peterlin, A. *Makromol. Chem.* 1964, **73**, 188
10 Barrie, J. A. and Platt, B. *J. Polym. Sci.* 1961, **54**, 261
11 Yasuda, H. and Peterlin, A. *J. Appl. Polym. Sci.* 1974, **18**, 531
12 Peterlin, A. *J. Macromol. Sci.* (*B*) 1975, **11**, 57
13 Levita, G. and Smith, T. L. to be published
14 Pasternak, R. A., Schimscheimer, J. F. and Heller, J. *J. Polym. Sci.* (*A-2*) 1970, **8**, 467
15 Ziegel, K. D., Frensdorff, H. K. and Blair, D. E. *J. Polym. Sci.* (*A-2*) 1969, **7**, 809
16 Caskey, T. L. *Modern Plastics* 1967, **45**(4), 148
17 Sternstein, S. S. and Ho, T. C. *J. Appl. Phys.* 1972, **43**, 4370
18 Myers, F. A., Cama, F. C. and Sternstein, S. S. in 'The Glass Transition and the Nature of the Glassy State', (Ed. Goldstein and Simha) *Ann. New York Acad. Sci.* 1976, **279**, p 94
19 Sternstein, S. S. in 'Treatise on Materials Science and Technology, Vol. 10, Part B, Properties of Solid Polymeric Materials', (Ed. Schultz), Academic Press, New York, 1977, p 541
20 Levita, G. and Smith, T. L. unpublished results
21 Amborski, L. E. *I&EC Prod. Res. Develop.* 1963, **2**, 189
22 Turnbull, D. and Cohen, M. H. *J. Chem. Phys.* 1961, **34**, 120
23 Ferry, J. D. 'Viscoelastic Properties of Polymers', 2nd Edn. Wiley, New York, 1970
24 Cohen, M. H. and Turnbull, D. *J. Chem. Phys.* 1959, **31**, 1164
25 Fujita, H. *Adv. Polym. Sci.* 1961, **3**, 1
26 Vrentas, J. S. and Duda, J. L. *J. Polym. Sci.* (*Polym. Phys. Edn*) 1977, **15**, 403
27 Chen, S. P. and Ferry, J. D. *Macromolecules* 1968, **1**, 270
28 Macedo, P. B. and Litovitz, T. A. *J. Chem. Phys.* 1965, **42**, 245
29 Tikhomirov, B. P., Hopfenberg, H. B., Stannett, V. and Williams, J. L. *Makromol. Chem.* 1968, **118**, 177
30 Ferry, J. D. and Stratton, R. A. *Kolloid Z.* 1960, **171**, 107
31 Matsuoka, S. and Ishida, Y. (a) *J. Polym. Sci.* (*C*) 1966, **14**, 247; (b) *Polym. Preprints* 1965, **6**, 795
32 McCrum, N. G., Read, B. E. and Williams, G. 'Anelastic and Dielectric Effects in Polymer Solids', Wiley, New York, 1967
33 O'Reilly, J. M. *J. Polym. Sci.* 1962, **57**, 429
34 O'Reilly, J. M. *J. Appl. Phys.* 1977, **48**, 4043
35 Mercier, J. P., Aklonis, J. J., Litt, M. and Tobolsky, A. V. *J. Appl. Polym. Sci.* 1965, **9**, 447
36 Michaels, A. S. and Bixler, H. J. *J. Polym. Sci.* 1961, **50**, 413
37 Chen, S. P. and Edin, J. A. D. *Polym. Eng. Sci.* 1980, **20**, 40
38 Yee, A. F. personal communication
39 Litt, M. H. and Torp, S. *Ind. Eng. Chem. Prod. Res. Develop.* 1972, **11**, 357
40 Simha, R. and Weil, C. E. *J. Macromol. Sci.* (*B*) 1970, **4**, 215
41 Litt, M. H. *Trans. Soc. Rheol.* 1976, **20**, 47