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Permeation of Gases in Polystyrene Molded at Elevated Pressures

Atactic polystyrene was molded at pressures up to 3000 atmospheres, and the effects of this pressure history were studied by permeability measurements using helium, neon, and argon as probe molecules. The permeabilities were significantly reduced by molding at higher pressures. The diffusion coefficients decreased monotonically with molding pressure, reflecting more extensive interchain cohesion. In contrast, the solubility coefficients showed a broad minimum around a molding pressure of 1000 atm, indicating that changes in local order were induced by higher pressures. These changes were shown to affect permeation, mechanical characteristics, and other properties. An optimum molding pressure somewhat below 1000 atm is indicated for polystyrene.

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SCOPE

The growing body of work concerned with modification of polymer properties under the application of elevated pressure, reviewed recently by O'Reilly (*1*), has confirmed that this thermodynamic variable can induce major changes in polymer properties. However, only a few introductory studies (*2* to *7*) have been made of the potentially important residual effects on amorphous polymers of a high-pressure history, such as high molding pressures. Studies of this type of behavior to date have been concerned almost entirely with the residual density increase, or volume compaction effect, and with its relaxation on heating or annealing. A wider variety of techniques must be used to characterize more fully the effects of a high-pressure history in order to establish reasonable structure-property relationships. We have conducted a more extensive characterization of the effects of kilobar molding pressures on a common system-polystyrene-glasses and have reported the changes in several mechanical and relaxation properties (*8*). The observed property variations indicated that the pressure history had a strong effect on the packing and stability of the polymer structure on a molecular scale.

Further information about the nature of the polymer microstructure is presented in this paper, where diffusion and solubility measurements of simple gases were used as a molecular probe, sensitive to changes in polymer order on a scale comparable to the size of the penetrant molecule. Such measurements can be made repeatedly using probe molecules of different sizes without perturbing the inherent sample properties. The results provide information of direct importance for packaging and selective membrane separation applications. In addition, the fundamental dependence of solution and transport processes on the detailed nature of polymeric materials (*9* to

11) allows one to deduce the nature of certain changes in polymer microstructure which are not accessible to any other experimental technique. Although exact quantitative relationships may not always be available, such information offers considerable insight into the dependence of properties on structure. The results indicate that excessively high molding pressures can introduce localized void-like defects and other variations in polymer microstructure which significantly influence gas permeation and other important properties of the polymer.

CONCLUSIONS AND SIGNIFICANCE

Polystyrene samples molded at 1000 atm and above had permeabilities to argon less than half that of compression molded control samples. The relative magnitude of the decrease in permeability with increasing molding pressure was observed to increase with increasing penetrant size. This suggests that the effectiveness of the polymer as a barrier to molecules larger than argon would be even more greatly enhanced by high pressure molding techniques.

The diffusion coefficients decreased monotonically with increasing molding pressure, with the relative magnitudes of decrease in the same order as the size of the penetrant molecules. Arrhenius activation energies for diffusion also were higher for high molding pressure. The dependence of diffusion coefficients on pressure was shown to follow a linear free energy relation. It is concluded that the increase in activation energy is caused by an increase in the thermodynamic internal pressure of the polymer, reflecting more extensive interchain cohesive forces in the pressure-molded samples.

The gas solubility coefficients, however, did not vary monotonically, but rather showed a broad minimum in the range of molding pressures around 1000 atm. This also was the region of molding pressure in which a maximum was observed previously in the compressive yield stress and where an exothermic relaxation process, detected by DTA measurements (*8*), appeared somewhat below T_g. These changes in solubility can be related to changes in the fraction of the polymer volume which is available to the gas for solution. A new expression was developed to represent this available volume fraction:

$$\phi_2 = \frac{s\, p_s\, T}{T_s} \exp\left\{\frac{\Delta H_{\mathrm{sol}}}{RT} + I\right\}$$

The derived quantity ϕ_2 includes both void space and liquid-like free volume. Calculated values of ϕ_2 decrease with increasing size of the penetrant molecule.

The solubility coefficients increased slowly as a given pressure-molded sample aged at room conditions. This is attributed to the formation of additional sorption sites as domains of localized strain energy relax to form a region of high local void volume.

These results indicate a rearrangement of segmental structure under pressure, involving compaction of the polymer matrix over the entire pressure range studied, with concurrent generation of sorption sites at higher molding pressures by the formation of noninterconnected voids as localized internal hydrostatic strains relax. The structural changes induced by increased molding pressures also have been found to affect stress-strain behavior, relaxational phenomena, and other physical properties (*8*).

It is apparent that a molding pressure near to or somewhat below 1000 atm should optimize the gas barrier properties, strength, and mechanical stability of polystyrene. This range of pressure is feasible in current commercial production equipment. It is anticipated that polymers other than polystyrene which are more sensitive to pressure compaction (*2*, *3*) may exhibit even greater changes in properties when molded under suitable high pressures. This general method of polymer modification may prove useful for the preparation of polymeric materials with desired solution, permeation, and mechanical characteristics for certain specific applications.

EXPERIMENT

The polymer used in the present work was Dow Styron 690, a thermally polymerized atactic polystyrene nominally free of any additives. The intrinsic viscosity was 0.88 $(\mathrm{g}/100\ \mathrm{cc})^{-1}$ measured in toluene at 25°C, corresponding to $\overline{M}_v \approx 240{,}000$. A $\overline{M}_w/\overline{M}_n$ ratio of about 2.3 is reported by the manufacturer for this polymer. The glass transition temperature at atmospheric pressure was 96°C, measured in a conventional glass dilatometer. The glass transition at high pressure was measured using a high-pressure steel dilatometer described elsewhere (*12*). Over the range from 1 to 1700 atm, the T_g increased at the rate of 0.030°C/atm. This was quite consistent with literature reports (*1*, *5*, *6*, *13*) that the T_g of polystyrene increases at an initial rate of 0.025-0.030°C/atm, and at a lower rate of about 0.015°C/atm at higher pressures in the range of 4000 to 6000 atm (*13*).

A mold was designed and built up to produce discs 8.5 cm in diameter at pressures up to 5000 atm. The molding faces could be reproducably aligned relative to each other to within ± 25 μm over the entire face area, so that the thickness of a given molding was quite uniform from point to point. The mold was evacuated during heating to devolatilize the polymer and protect the sample against oxidative degradation. The samples were molded as sheets of thickness l of about 0.5 mm. The appropriate amount of polymer was heated to 200°C in the mold under no load, then a small load was applied to deform the polymer and fill the available space. The pressure was then raised to the desired high pressure level over a period of about one minute. After an appropriate dwell time under pressure as discussed below, the heater was shut off and the mold cooled in free air at a few degrees per minute under constant pressure. When the mold had cooled below 30°C, the pressure was released and the sample transferred to the gas transmission cell.

The dwell times of 3 to 15 minutes for the polymer under pressure were calculated to be at least one order of magnitude longer than the relaxation time τ predicted by the WLF equation. The absence of birefringence in the plane of the cooled samples indicated that the dwell times were sufficient for relaxation under the conditions used. The density of the high-pressure moldings was about 1% greater than that of the controls, but the scatter in the measurements was greater than permissible for use as a characterization parameter.

Gas permeation properties were measured using high purity (99.9 + %) helium, neon, and argon as probe molecules. The experimental method was an adaptation of the high-vacuum technique described by Barrer and Skirrow (*14*). The sample, supported by a porous plate of sintered stainless steel, was mounted in a diffusion cell to partition it into two chambers. The sample and cell were thoroughly evacuated, then at time $t = 0$, a known pressure, p_1, (about 50 cm Hg) of the desired gas was admitted to one side of the cell while essentially zero pressure was maintained at the other surface of the sample. The increase with time of the pressure in the constant-volume reservoir on the low-pressure side of the sample was measured with a sensitive diaphragm-type differential pressure transducer and recorded continuously on a time base into the region of steady state permeation. The steady state pressure increase in the reservoir was extrapolated into the time axis to give the time lag L and the diffusion coefficient was calculated by the well-known relation (*9* to *11*):

$$D = \frac{l^2}{6L} \tag{1}$$

The permeability coefficient was calculated from the steady state flux J by

$$\underline{P} = \frac{J}{p_1/l} \tag{2}$$

By identity, the solubility coefficient is

$$s = \underline{P}/D \tag{3}$$

The gas transport properties showed some dependence on the time elapsed since molding, as discussed in a later section. This relaxation effect was standardized by evacuating the samples for at least four days at 25°C before taking any data except those directly relating to the initial sample aging effects. After that interval, the change in permeation properties with linear time was quite slow (less than 1/2 % per day) compared to the time scale of the measurements. Data for determination of the activation energies and heats of solution were taken in the range from 0°C to 25°C; after molding, the samples were not exposed to temperatures higher than 25°C in order to minimize the relaxation effects.

RESULTS AND DISCUSSION

The permeability, diffusion, and solubility data for the different molding pressure conditions are given in Table 1. The reproducibility of the data was usually ±3% or better. These data show that significant reductions in transport and solubility are achieved by an increase in the molding pressure. For example, the permeability to argon is reduced in each of the higher pressure molded samples to well below half that of the control (50 atm) sample. The observed trend for relatively greater reductions in permeability with increasing atomic size of the penetrant suggests that the decrease in film permeability would be even greater for larger size molecules than were used in this study. This change in film barrier properties could be of considerable significance for certain practical packaging or separation process applications.

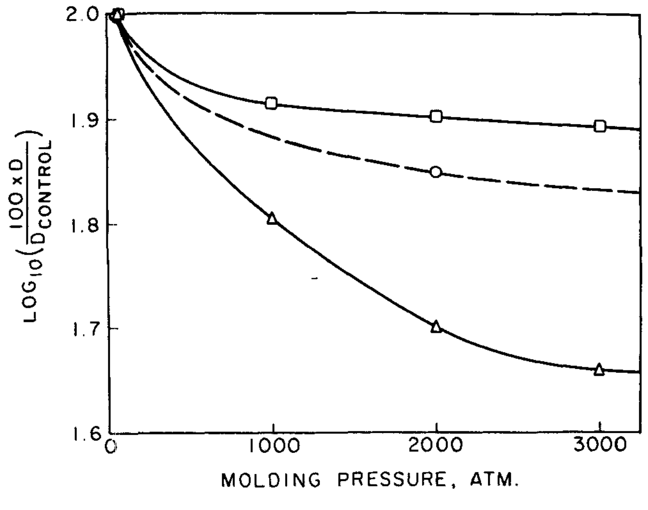

Fig. 1. Logarithm (normalized by vertical shift) of diffusion coefficient at 25°C as a function of vitrification pressure of polystyrene glass. Penetrants are (□) helium, (○) neon, and (△) argon.

The nature of these changes in transport properties and their dependence on the pressure-induced changes in polymer structure are more easily understood by consideration of the corresponding variations in the diffusion and solubility coefficients. The permeability coefficient is the composite of these two more fundamental parameters which relate to the kinetic and thermodynamic characteristics of the polymer-penetrant mixture.

Diffusion

The changes of the diffusion coefficients relative to the control (50 atm) values at 25°C are shown as a function of vitrification pressure in Figure 1. For each gas, the value of D decreased monotonically as the vitrification pressure was increased. The magnitude of the relative decrease became larger as the size of the probe molecule increased in the order: He, Ne, Ar.

Table 2 lists the apparent Arrhenius activation energies for diffusion in the samples molded at 2000 atm and at 50 atm. It is seen that the activation energies are higher for the high-pressure sample. The values of D_0 in the Arrhenius equation [Equation (5)], although not shown here, are also higher for the high-pressure sample. When the values of log D at 25°C were plotted against E_d, as shown in Figure 2, it was seen that seven points from three moldings and three penetrants were well described by a single straight line:

$$\log_{10}(D_{25^\circ\mathrm{C}}) = -3.65 - 0.46\,E_d \tag{4}$$

From this observation, it is possible to interpret the behavior of the diffusion coefficient in some detail by comparing the Arrhenius and Eyring expressions for the diffusion coefficient and a recast form of Equation (4), respectively:

$$\ln D = \ln D_0 - \frac{E_d}{RT} \tag{5}$$

$$\ln D = \ln\left[\frac{\epsilon kT}{h}\lambda^2\right] + \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT} \tag{6}$$

$$\ln(D_{25^\circ\mathrm{C}}) = -9.0 + \frac{\left(\frac{0.38}{298}\right)\Delta H^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT} \tag{7}$$

Figure 2 demonstrates the linear free energy relation described by Barrer and Skirrow (*14*, *15*), Kwei and Arnheim (*16*), Lawson (*17*), and others. For a large number of polymer-penetrant systems, most of them above T_g, these investigations have found that ln D_0 (and hence ln D) is a linear function of E_d/T. Since the term $\epsilon kT\lambda^2/h$ is not widely variable, the relation implies that $\Delta S^\ddagger$ is linearly related to $\Delta H^\ddagger$ (or to E_d, since $E_d = \Delta H^\ddagger + RT$). The specific relation proposed by Lawson is

$$\Delta S^\ddagger = 4\alpha\Delta H^\ddagger \tag{8}$$

TABLE 1. SUMMARY OF GAS PERMEATION IN POLYSTYRENE GLASSES MOLDED AT HIGH PRESSURES

Molding pressure,	Gas	Temp., °C	Permeability coeff. × 10^{11} $\left(\frac{cc\ (STP)}{cm^2\text{-sec-cmHg/cm}}\right)$	Diffusion coeff. × 10^8 $\left(\frac{cm^2}{sec}\right)$	Solubility coeff. × 10^5 $\left(\frac{cc\ (STP)}{cc\text{-cmHg}}\right)$
50 atm	He	25	315	1,151	27.3
50 atm	He	0	182	730	25.0
50 atm	He	10	231	870	26.6
50 atm	He	20	285	1,044	27.3
50 atm	He	20	286	1,070	26.8
50 atm					
50 atm	Ne	25	82.8	198	41.8
50 atm	Ne	25	81.6	197	41.5
50 atm	Ne	25	81.3	196	41.4
50 atm	Ne	0	44.8	112	39.8
50 atm	Ne	5	48.9	114	42.7
50 atm	Ne	10	56.7	134	42.2
50 atm	Ne	20	75.7	178	42.4
50 atm	Ar	25	21.5	5.17	416
50 atm	Ar	25	21.6	5.36	404
50 atm	Ar	5	11.8	2.03	580
1000 atm	He	25	202	945	21.4
1000 atm	He	25	196	956	20.5
1000 atm	He	25	223	930	24.0
1000 atm	Ar	25	9.00	3.53	255
1000 atm	Ar	25	9.89	3.19	310
2000 atm	He	25	194	919	21.1
2000 atm	He	6	126	634	19.9
2000 atm	He	10	136	682	20.0
2000 atm	He	15	155	733	21.1
2000 atm	He	20	172	845	20.4
2000 atm	Ne	25	44.4	139.3	31.9
2000 atm	Ne	6	27.1	81.4	33.3
2000 atm	Ne	10	30.0	92.6	32.4
2000 atm	Ne	15	34.0	108.9	31.3
2000 atm	Ne	20	39.4	121.3	32.5
2000 atm	Ar	25	8.47	2.65	319
2000 atm	Ar	25	8.32	2.65	314
2000 atm	Ar	10	5.13	1.22	422
3000 atm	He	25	206	862	23.9
3000 atm	He	25	206	860	23.9
3000 atm	He	0	118	567	21.0
3000 atm	He	0	119	554	21.5
3000 atm	He	13	166	713	23.2
3000 atm	He	13	165	715	23.1
3000 atm	Ar	25	8.31	2.46	338
3000 atm	He	25	8.70	2.36	366

where α is the volume coefficient of thermal expansion.

If the linear free energy analysis is correct, it should be possible to estimate α from diffusion measurements alone. The present data yielded the value $\alpha = 3.2 \times 10^{-4}/°C$, in good agreement with the literature value for polystyrene of $2.7 \times 10^{-4}/°C$[18]. The value of the ratio $\Delta S^{\ddagger}/4\ \Delta H^{\ddagger}$ was in fact much closer to the dilatometrically measured α than was any of the values calculated in Lawson's paper. While such agreement may be fortuitous, it also may be due to the fact that polystyrene at 25°C shows much less viscous relaxation (on a macroscopic scale) than did any of the samples considered by Lawson, who used primarily data taken above T_g. Since much of Lawson's treatment was based on the behavior of an elastic medium, it might be expected that liquid-like relaxation would be a major complication.

TABLE 2. APPARENT ACTIVATION ENERGY FOR DIFFUSION (E_d) AND HEAT OF SOLUTION (ΔH_{sol} FOR GASES AT 25°C IN POLYSTYRENE MOLDED UNDER DIFFERENT PRESSURES

Gas	E_d (kcal/mole) 50 atm	E_d (kcal/mole) 2000 atm	ΔH_{sol} (kcal/mole) 50 atm	ΔH_{sol} (kcal/mole) 2000 atm
He	3.0	3.3	0.57	0.48
Ne	4.4	4.6	−0.21	−0.26
Ar	7.8	8.7	−2.9	−3.2

The above analysis and the observation that both moldings in Figure 2 fall on the same line indicate that if the (irreversible) pressure compaction effect could be eliminated in the conventional dilatometer, then the reversible part of the thermal expansion coefficient would be much the same in the high-pressure sample as in the control. This was assumed in Gee's thermodynamic analysis (*6*) and indicated by the results of Shishkin (*2*) and

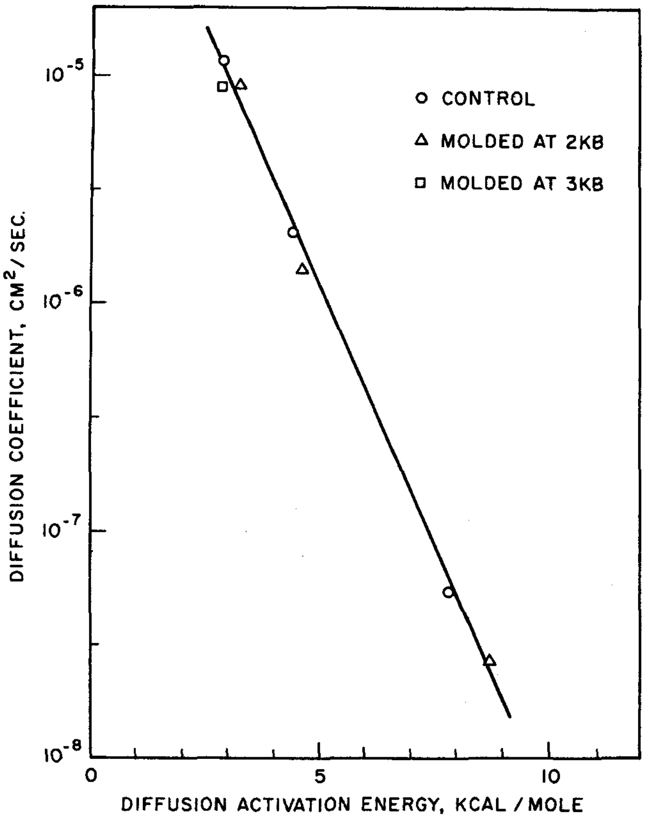

Fig. 2. Diffusion coefficient at 25°C vs. diffusion activation energy for helium, neon, and argon in polystyrene glasses vitrified at (○) about 50, (△) 2000, and (□) 3000 atmospheres.

Saito (*4*). It is noted also that the present samples showed a very definite linear free energy relationship for a glassy polymer and that diffusion of a molecule as small as helium occurred in this case by the same general activated process as for larger molecules—two aspects which did not necessarily hold in the previous studies cited.

It seems evident from these results that the lower diffusion coefficients in the pressure-molded samples are the result of a single uniform change in polymer properties which causes the increase in the jump activation enthalpy and a proportional increase in activation entropy. In the interpretation of the activation energy for diffusion, it is generally agreed that the major contribution arises from the energy required to separate the chains against the forces of interchain cohesion. Mathematical models for the activation enthalpy are dominated by the product of one factor representing the cohesive forces of the polymer multiplied by a factor related to the local volume involved in the diffusion jump. Meares (*19*) and Kwei and Arnheim (*16*), among others, have interpreted the activation enthalpy as being determined primarily by the product of the thermodynamic internal pressure of the polymer $\left[P_i = \left(\frac{\partial U}{\partial V} \right)_T = T\frac{\alpha}{\beta} - P \right]$ times the cylindrical volume swept out by a penetrant molecule of diameter d making a diffusive jump of length λ, $\left(\frac{\pi d^2 \lambda}{4} \right)$. Their data clearly showed a linear relationship between the activation enthalpy and the square of the penetrant diameter. Other relations have been suggested, but a second-power dependence on d accounts for the majority of cases (*16*), and in any case, the exact relation between $\Delta H^{\ddagger}$ and the gas diameter is not critical to the present argument. A plot of E_d versus $\pi d^2\lambda/4$ in Figure 3 shows this linear relationship for the present samples. The penetrant diameters are literature values calculated from gas viscosities (*16, 19, 20*).

The relationship between $\Delta H^{\ddagger}$ and d^2 is also shown in the above references to be nearly simple proportionality for polystyrene and most polymers, so the plots of E_d vs. d^2 should intersect the ordinate at a common value near RT. Figure 3 has been drawn to reflect this. The slope for the 2000 atmosphere molding is higher than that for the control sample, by about 10%. The increase in the proportionality constant must be attributed to an increase in the term "$P_i\lambda$." It is not possible to separate these factors analytically without determining P_i, for example, by measuring the P-V-T surface of the pressure-compacted sample in such a way that the compaction effect does not relax. However, it seems highly unlikely that the jump length would have increased in the more dense medium. If it had, this would have tended to separate the data in Figure 2 into separate lines for each molding, since λ^2 appears in the pre-exponential factor of the Eyring equation for the diffusion coefficient.

It was concluded from the diffusion data then that the increased activation energy is caused by an increase in the internal pressure of the polymer, reflecting more extensive interchain secondary bonding. It might be expected that both the number of secondary bonds and possibly the effective strength of the average bond would be increased by the high-pressure molding, but no information is available to separate these two effects. Gee's

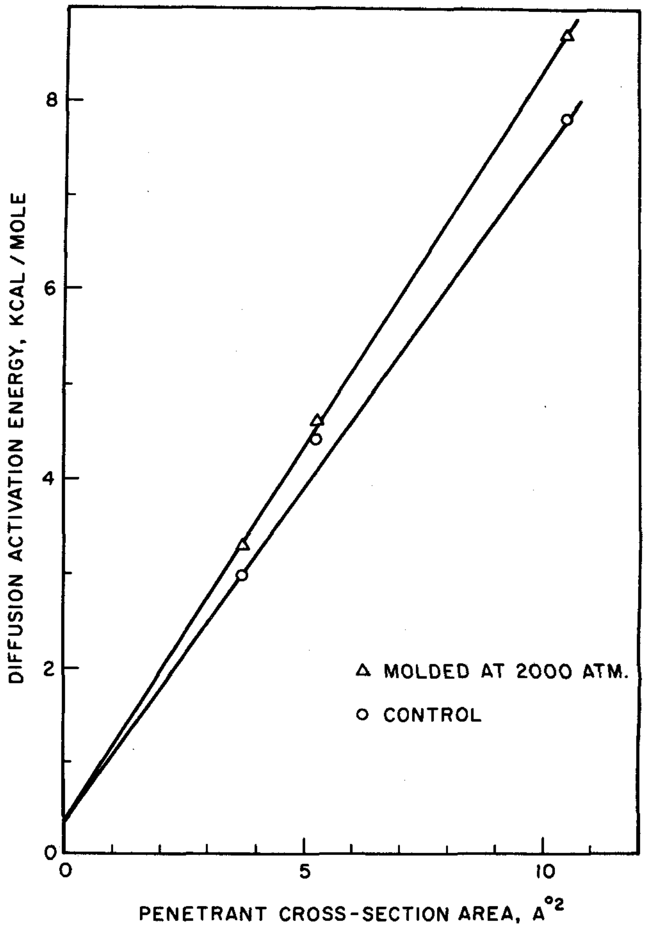

Fig. 3. Diffusion activation energy vs. cross-sectional area of penetrant molecule for polystyrene glasses vitrified at (△) 2000 atmospheres, and (○) control.

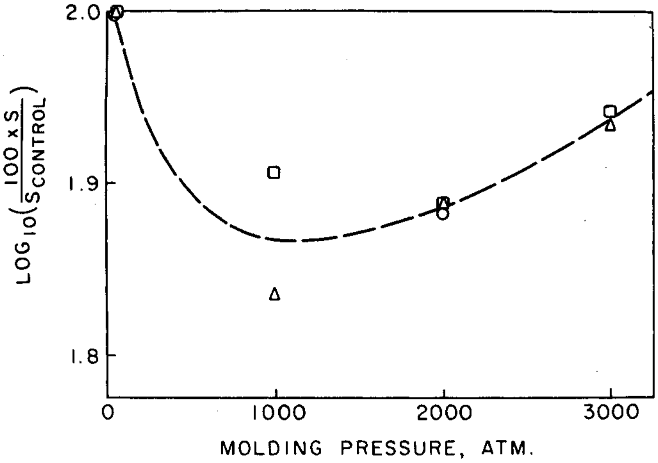

Fig. 4. Logarithm (normalized by vertical shift) of solubility coefficient at 25°C as a function of vitrification pressure of polystyrene glass. Penetrants are (□) helium, (○) neon, and (△) argon.

thermodynamic analysis (*6*) supports the conclusion that the internal pressure of polystyrene is increased by vitrifying under pressure. The present pressure-molded samples also showed a lower mechanical damping factor than the controls and a higher elastic modulus (*8*). This also indicates that intermolecular binding forces are stronger or more numerous in the high-pressure structure.

Solubility

The normalized logarithms of the solubility coefficients at 25°C are shown in Figure 4 for the three probe gases as a function of vitrification pressure. In marked contrast to the diffusion coefficients, a broad minimum in solubility is seen at molding pressures around 1000 atmospheres. The region of molding pressure corresponding to the minimum coincides fairly well with that of an observed maximum in the compressive yield stress of the samples, and with the appearance of an exothermic relaxation process seen somewhat below T_g by differential thermal analysis (*8*). The heats of solution are shown in Table 2, and appeared to be slightly more exothermic for the pressure-molded samples.

For purposes of analysis, the solubility coefficient may be considered to be determined by two factors. One is the relative strength of polymer-penetrant interaction forces compared to polymer-polymer forces, as measured by the heat of mixing. Other factors being equal, a more exothermic heat of mixing will result in a larger solubility coefficient. The other factor is the number of available sites in the polymer where the gas can dissolve. In a liquid, these sites can arise simply from statistical density fluctuations, but in a glassy polymer they may be fixed physical entities. Studies of the solution of small molecules in polystyrene and poly(vinyl acetate) glasses have strongly indicated that sorption occurs in preferred regions variously called *microcapillaries* (*21*), *microvoids,* or *holes* (*22*) or regions of reduced cohesive energy density (*19, 23*), which are related to variations in packing or local structure. The number and total volume of these sorption sites would quite likely be affected by the pressure history of the sample, and, as indicated by the solubility coefficient, appeared to pass through a minimum as the molding pressure was raised.

We therefore undertook to develop a more quantitative estimate of the polymer volume available to the gas for solution. The equation we suggest for this quantity is based on a modification presented below of an equation by Gee for the solubility of gases in rubbers (*24*):

$$L_b\left(\frac{T}{T_b}-1\right)+RT\left[\ln\left(\frac{s\,p_s V_1}{V_s}\right)+1\right]+\Delta H_{\mathrm{mix}}=0 \quad (9)$$

Gee derived Equation (9) based on the (net zero) change in free energy as the penetrant gas condensed to a (hypothetical) liquid at the temperature of the experiment, and mixed with the rubber. The quantity

$$-R\left[\ln\left(\frac{s\,p_s V_1}{V_s}\right)+1\right]$$

represents the partial molar entropy of the penetrant dissolved in the rubber, as calculated by the Flory-Huggins theory of polymer solutions (*25*). This expression for $\Delta\overline{S_1}$ is not applicable to a glassy polymer, however, since the Flory-Huggins theory assumes that chain segments may rearrange to accommodate a penetrant molecule at any random site on the lattice. This assumption is unwarranted in the glassy state, especially in light of the evidence cited above for preferred sorption sites. It may be possible to modify the Flory-Huggins entropy calculation to account for the situation in the glassy state by some combination of introducing empty cells and/or mathematically immobilizing some part of the polymer. However, there is another approach which is more readily calculable as a description of the case.

Hildebrand (*26*) cites objections to the lattice treatments, and instead treats the liquid as similar in some respects to a dense real gas. His description of mixing is in terms of free volume, by which the partial molar entropy may be written:

$$\Delta\overline{S_1}=-R\left[\ln\left(\frac{\phi_1 N_1 V_1}{\phi_1 N_1 V_1+\phi_2 N_2 V_2}\right)+I\,\frac{N_2(\phi_2 V_2-\phi_1 V_1)}{\phi_1 N_1 V_1+\phi_2 N_2 V_2}\right] \quad (10)$$

Hildebrand calculates the free volume of a liquid from its entropy of vaporization by

$$\Delta S_{\mathrm{vap}}=R\ln\left[\frac{V^f{}_{\mathrm{gas}}}{V^f{}_{\mathrm{liq}}}\right] \quad (11)$$

At room conditions, $V^f{}_{\mathrm{gas}}$ is virtually equal to V_{gas}. Equation (10) differs slightly from Hildebrand's expression in that the molar free volume V^f has been rewritten for convenience as ϕV, where ϕ is a (dimensionless) free volume fraction. Also, it might be argued in the present case that while the penetrant is mobile enough to mix completely into the local free volume of neighboring polymer, some segments of the polymer may not be mobile enough to mix completely into the free volume of the sorbed penetrant, that is, the mixing of polymer and penetrant does not lead to the creation of a homogeneous solution, due to the inherent immobilization of polymer in the glassy state. To allow for this possibility, an efficiency factor I has been inserted in the final term of Equation (10) to reflect the extent of mixing of the polymer with the free volume of the penetrant. Without more specific information, however, I will be taken to be unity for the present. It also will be noted that Equation (10) reduces to the Flory-Huggins expression for $\Delta\overline{S_1}$ as a special case if one assumes $\phi_1=\phi_2$, which is implicit in the Flory-Huggins theory.

Equation (10) can be simplified for the present data by noting that the free volume of the polymer dominates the equation. N_2/N_1 is never much less than unity, and

$V_2/V_1 \approx 10^4$, so if ϕ_2/ϕ_1 is not much less than 10^{-3}, (which will prove to be the case), Equation (10) reduces to

$$\Delta\bar{S}_1 = -R\left[\ln\left(\frac{\phi_1 v_1}{\phi_2}\right) + I\right] \qquad (12)$$

where v_1 is the volume fraction of the penetrant in the mixture and

$$v_1 = \frac{s\, p_s\, V_1}{V_s} \qquad (13)$$

Equations (12) and (13) can replace the partial molar entropy term in Equation (9) to obtain a gas solubility equation which is more applicable to the glassy state. However, further simplification is possible by noting that the term $L_b T/T_b$ in Equation (9) represents the entropy contribution to the free energy of condensation at the experimental temperature. Comparing that term and Equation (11) for the entropy of vaporization, one obtains

$$\frac{L_b T}{T_b} = RT\ln\left[\frac{V_s T/T_s}{\phi_1 V_1}\right] \qquad (14)$$

Also, the heat of mixing is the sum of the observed heat of solution plus the heat of vaporization of the penetrant

$$\Delta H_{\text{mix}} = \Delta H_{\text{sol}} + L_b \qquad (15)$$

When these substitutions are made into Equation (9) and the result is rearranged, a simple expression for ϕ_2 is obtained which is a convenient and somewhat novel measure of the volume of available sorption sites in the glassy polymer

$$\phi_2 = \left(\frac{s\, p_s\, T}{T_s}\right)\exp\left(\frac{\Delta H_{\text{sol}}}{RT} + I\right) \qquad (16)$$

The pre-exponential term ($s\ p_s\ T/T_s$) is the Ostwald solubility coefficient, which represents the volume at the experimental conditions of the gas that will dissolve in a unit volume of polymer. It can be shown easily that Equation (16) still holds as written if the actual gas pressure p_1 is different from p_s or if the conditions of STP are arbitrarily chosen to be different from the conventional ones. Although Equation (16) was developed from a liquid model, inspection shows that it also has a meaning in the opposite extreme where the polymer is regarded as an inert sponge of voids and solid material. In that case $\Delta H_{\text{sol}} = 0$, and since the sponge is inert, $I \equiv 0$. Then $\phi_2 = s\ p_s\ T/T_s$ which is simply the void fraction of the sponge. Although it is necessary, in the general case, to assume a value for I (we have used $I = 1$), this uncertainty can change the calculated ϕ_2 by no more than a factor of e, which is small compared to the range of ϕ_2. Since ϕ_2 includes both void space and liquid-like free volume, it is referred to as an available volume fraction.

Values of the available volume fraction calculated for the present samples are presented in Table 3. It is seen that ϕ_2 decreased as the penetrant size increased, which would be expected as successively larger limits would be placed on the smallest space penetrable by a given gas. Also for each gas, the available volume is seen to be smaller in the 2000 atmosphere molding than in the control. The data for helium indicate that this more quantitative measure of the volume available for solution goes through a minimum in much the same way as does the solubility itself.

The minimum in solubility or available volume is interpreted to be the result of two competing processes. Since sorption in glassy polystyrene occurs partially in packing defects of some sort, as cited above, it is expected that a portion of these are squeezed out or rendered thermodynamically unfavorable as the molding pressure is increased to about 1000 atmospheres. At higher molding pressures, however, some process resulting in the introduction of defects becomes dominant, and the number of sorption sites increases. This increase is seen in terms of the formation within the polymer of a second structure which is highly dispersed, or has a high local void volume. Such a dispersed structure may be related to relaxation of localized strain domains upon decompression of the sample (27). Since the diffusion coefficient continues to decrease for molding pressures above 1000 atmospheres, these pressure-induced defect regions cannot occupy a large fraction of the total polymer volume, nor are they interconnected into channels through the sheet.

TABLE 3. VALUES OF AVAILABLE VOLUME FRACTION, ϕ_2, FOR GASES IN POLYSTYRENE

Gas	Molding pressure control	2000 atm	3000 atm
Helium	0.16	0.11	0.18
Neon	0.065	0.046	
Argon	0.0074	0.0032	

Since the diffusion coefficient will be most strongly affected by regions of lowest defect content and segmental mobility, and the solubility coefficient will reflect most strongly regions of high defect content and mobility, it is not inconsistent that the two properties should change in opposite directions as the vitrification pressure is raised above 1000 atmospheres. It does, however, emphasize the heterogeneous nature of the system.

An effect of sample age on gas transport properties of the sample molded at 2000 atmospheres was also noted. The diffusion coefficient was virtually constant as the sample aged, but the solubility coefficient increased by some 20% over the period from 2 hours to 200 hours after the molding pressure had been released and was roughly linear with the logarithm of time. This indicates that additional sorption sites were being formed as the sample aged at room conditions. This was part of a relaxation process which was observed by other techniques at times up to six months after decompression. To minimize this effect, data were taken in the time interval of 100 to 300 hours, where the change in solubility with linear time was slow (less than 1/2% per day). It is recognized, however, that the glassy state, particularly a glass formed under high pressure, cannot be considered to be in complete thermodynamic equilibrium.

These results indicate that the higher molding pressures cause a rearrangement of polymer segmental structure involving compaction of the polymer matrix with concurrent generation of sorption sites at sufficiently high pressures by formation of noninterconnected regions of reduced density. These regions, corresponding to isolated domains of relatively high local void volume, are generated by relaxation of domains of high strain energy resulting from the high pressure-temperature molding process.

It may be expected that other types of polymers, which are more sensitive to pressure compaction (2, 3) than is polystyrene, could exhibit even more pronounced changes in transport properties when molded under sufficiently high pressures. This general method for modification of polymer structure and properties could prove to be useful for the preparation of polymeric materials with characteristics desirable for certain specific applications.

NOTATION

D = diffusion coefficient, cm^2/s
D_0 = pre-exponential term in Arrhenius equation for D
E_d = Arrhenius activation energy for diffusion jump, Kcal/mole of jumps
ΔH_{mix} = heat of mixing, Kcal/mole dissolved penetrant
ΔH_{sol} = heat of solution, Kcal/mole dissolved penetrant
$\Delta H^\ddagger$ = activation enthalpy of diffusion jump, Kcal/mole of jumps
I = efficiency with which polymer shares the free volume of the dissolved penetrant, dimensionless
J = mass flux through polymer sheet, cc gas at STP/cm^2-s
L = time lag at which steady state portion of gas transmission curve extrapolates into time axis, s
L_b = molar latent heat of vaporization, Kcal/mole
$\bar{M}_v$ = viscosity-average molecular weight, g/mole
N = number of moles of a component in a solution
$\underline{P}$ = permeability coefficient, cc gas at STP/cm^2-s-cmHg/cm
P_i = thermodynamic internal pressure, atm (or cal/cc)

$$P_i = \left(\frac{\partial U}{\partial V}\right)_T = T\frac{\alpha}{\beta} - P$$

R = universal gas constant, cal/mole-°K
$\Delta S^\ddagger$ = activation entropy of diffusion jump, cal/mole of jumps-°K
$\Delta \bar{S}_1$ = partial molar entropy of penetrant in solution, cal/mole-°K
ΔS_{vap} = entropy of vaporization, cal/mole-°K
T = temperature, °K or °C
T_b = normal boiling point of penetrant
T_g = glass transition temperature of polymer
T_s = standard temperature of STP
U = thermodynamic internal energy, Kcal/mole
V = volume, cc/mole
V^f = free volume of a component in a solution
V_0 = molar volume of the liquified penetrant
V_s = molar volume of gas at STP
d = diameter of penetrant molecule, cm or Å
h = Planck's constant
k = Boltzmann's constant
l = thickness of sample sheet, cm
s = gas solubility coefficient, cc gas at STP/cc polymer-cmHg
t = time since start of experiment, s
p = penetrant pressure, cmHg
p_1 = pressure on upstream side of permeation sample
p_s = standard pressure of STP
v = volume fraction of a component in a solution

Greek Letters

α = isobaric volume coefficient of thermal expansion, °C^{-1}
β = isothermal compressibility, atm^{-1}
ϵ = transmission efficiency coefficient in Eyring equation
λ = average length of diffusion jump, cm or Å
ϕ = free volume fraction, dimensionless. $\phi = V^f/V$
ϕ_2 = "available volume fraction" of polymer

Subscripts

1 refers to penetrant
2 refers to polymer

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