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Selectively Permeable Polymers and Gas-separation Membranes: Structure and Transport Properties

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The relationship between the permeability coefficients and the sorption and diffusion properties of highly elastic and vitreous polymers has been examined. The concept of free volume can be used to interpret the characteristics of transport not only in highly elastic but also in vitreous polymers. The properties are discussed of the basic polymeric materials of gas-separation membranes; heterophase polymeric systems such as block copolymers and polymers with liquid-crystalline additives and additives undergoing specific interaction, and also quasi-liquid membranes with components facilitating the transport of gases. The bibliography contains 84 references.

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I. INTRODUCTION

The considerable progress made in the last ten years in the field of membrane gas-separation has been the result of the development of a number of membranes characterised by high efficiency and selectivity combined with stability of their properties in the media being separated. A high efficiency can be achieved by producing a definite "architecture" of the membrane as a polymeric solid or by selecting for the membrane a polymeric material characterised by high diffusion and sorption parameters. Most frequently, these two approaches are combined.

The gas-permeability coefficients of polymers may differ by 5–6 orders of magnitude, depending on their structure, whereas for comparison, in liquids, the values vary by only 1–2 orders of magnitude. This is due to the varied structural characteristics of the polymeric materials and the marked influence of the structure of the polymer on the rate of gas transfer. It is thus possible to ensure that the polymeric membranes have the required permeability and selectivity by influencing the structure of the polymer. At the same time, a characteristic compensation effect has been shown to exist: the most selective polymers have a low permeability, and highly permeable polymers are insufficiently selective or have poor mechanical and film-forming properties.[1-3]

The traditional approach to the analysis of the permeability and selectivity of non-porous gas-separation membranes involves the resolution of the diffusion and thermodynamic components of the permeability coefficients P_i and the separation factors $\alpha_{ij} = P_i/P_j$:

$$\alpha_{ij} = P_i/P_j = \sigma_i D_i/\sigma_j D_j = \alpha_{ij}^{\sigma}\alpha_{ij}^{D} \qquad (1)$$

The wide range of variation in the gas-permeability coefficients of polymers, noted above, is determined chiefly by the range of their diffusion properties. The sorption parameters, characterising the thermodynamic component of the permeability coefficient, differ to a much smaller extent for different polymers. It is traditionally assumed that the driving force of the mass transfer of simple gaseous molecules, and the concentration or activity gradient, is due to van der Waals intermolecular interaction. At the same time, a marked and selective increase in the permeability may be expected if any components of the mixture being separated undergo stronger specific interactions with the membrane material (electron donor–acceptor interactions, reversible coordinate bonding in a complex, and hydrogen bond formation).

With allowance for these characteristics of mass transfer in membranes and the requirements which they must satisfy, attention will subsequently be concentrated on the progress made in the development and application of polymeric materials in gas-separation membranes, and an attempt will be made to indicate the most promising apparent routes for the development of membrane science.

II. DIFFUSION AND FREE VOLUME IN POLYMERS

1. Highly Elastic Polymers

Polymers with high diffusion coefficients are attracting attention as materials for selectively permeable gas-separation membranes. The diffusion coefficients of gases depend on various properties of the polymer—density, presence and frequency of cross-linkages, degree of crystallinity, nature of the substituents, nature of the interchain interactions, and many others, but a direct correlation between these characteristics and the diffusion coefficients of gases can be observed only for a limited number of structurally similar series of polymers. With wide variation in the chemical character of the polymers, the diffusion coefficients show a statistically significant correlation only with the vitrification (glass) temperature T_g or the difference between the temperature of the measurement of the diffusion coefficient T_m and the glass temperature, $T_m - T_g$. This difference is sometimes regarded as a measure of the kinetic rigidity of the macro-chain. The relationship between the diffusion coefficients D at a given T_m and the glass temperatures

$$\lg D = A + BT_g, \quad (B<0)$$

was first noted in Ref.4. In Ref.4, however, this relationship was established only for a limited number of combinations of the diffusing substances and polymers with $T_g < 298$ K (rubbers and

partly crystalline polyalkenes). The universal character of Eqn.(2) for the highly elastic range was subsequently confirmed[5] by an analysis of published data[6,7] for a large number of polymers and gases. Fig.1 shows that with increase in temperature in the highly elastic range (left-hand branches of the curves), both the diffusion coefficients and the permeability coefficients decrease.

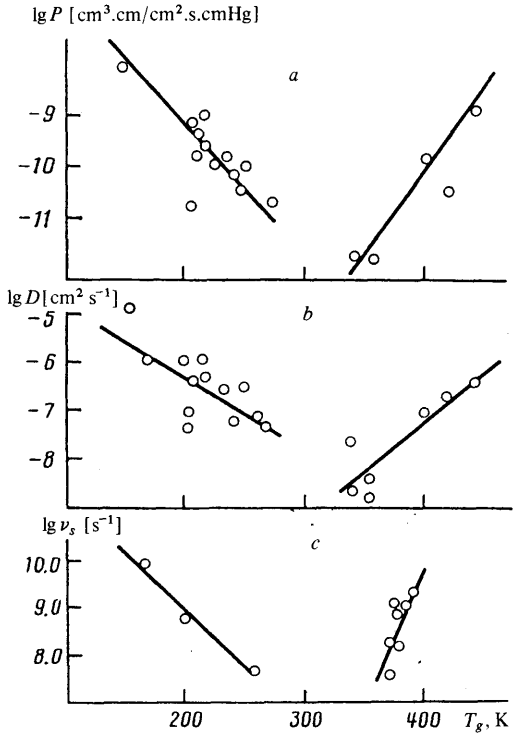
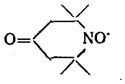


Figure 1. Correlation of the permeability coefficients of nitrogen (*a*), the diffusion coefficients of nitrogen (*b*), and the frequencies of rotation of the spin probe



ν_s (*c*) with polymer glass temperatures (from published data[6,7]).

The coefficient of translational diffusion of a gas in a polymer is an integral quantity, which may depend both on the local properties of the polymer and on its morphology (the sinuosity of the diffusion paths in the membrane, the presence of supermolecular structures, etc.). It is therefore extremely interesting to note the analogous decrease, with increasing T_g in the highly elastic range, in the coefficients of rotational diffusion of spin probes in polymers[5] (Fig.1). This shows that the observed decrease in D is related chiefly to the local mobility of the polymer chains. The fact that the diffusion coefficients of gases in rubbers, like the parameter of the Williams–Landel–Ferry equation a_T,[8] can be expressed as a single-valued function of T_g or the difference $T_m - T_g$ agrees with the view that the diffusion of gases in polymers at $T_m > T_g$ is determined chiefly by the segmental mobility

Since the free volume in rubbers is predominantly fluctuational in character, it is not surprising that different versions of the theory of free volume have been used successfully to describe the diffusion of gases in polymers at temperatures above T_g. The theory of free volume is based on the view that in a polymer, as in a liquid, there exists a free volume, whose elements, as a result of the random movement of the kinetic units making up the polymer, are displaced in space, and this makes possible the diffusion of small dissolved molecules or the viscous flow of the macromolecules in the polymer. According to the Cohen–Turnbull model of the free volume,[9] the diffusion coefficient can be represented as

$$D = A\mathscr{P}(v^*, v_f) = A \exp(-\gamma v^*/v_f) \qquad (3)$$

where $\mathscr{P}(v^*, v_f)$ is the probability that a molecule with a volume v^* enters a cavity with a volume $v > v_f$; γ is the overlap coefficient of the elements of the free volume, $0.5 < \gamma < 1$ (for simplicity, it can be taken as equal to 1); and A a constant.

In this simple form, however, the model cannot easily be used for the numerical estimation of diffusion coefficients in polymers. Various modifications of the model,[10–12] differing in the ways in which the dependence of v_f on temperature and the concentration of the diffusing substance is given, make it possible to use the thoery to describe the diffusion of organic solvents in rubbers. Subsequent refinement of the model of free volume led to the equation:[10,13,14]

$$D = RTA_d \exp(-B_d/v_f) \qquad (4)$$

where B_d characterises the volume of the substance diffusing, and A_d is a constant.

In this equation, the free volume v_f is given as a function of the temperature and pressure, that is it depends on the coefficient of thermal expansion of the polymer α and its compressibility β, and on a coefficient δ which allows for the influence of the diffusing substance on v_f (that is plasticising effects). Since the values of α and β for many polymers are known, for a complete description of the diffusion of gases it is sufficient to know the parameters A_d, B_d, and δ. This has been demonstrated for the transfer of CO_2, CH_4, C_2H_4, and C_3H_8 through polyethylene membranes at high pressures. The dependence of the permeability coefficient on the pressure (p_m) can be described by the equation:[14]

$$\ln \bar{P}(p_m) = \ln[\sigma_0 RTA_d \exp(-B_d/v_f)] + (B_d/v_f^2)(\delta\sigma_0 - 2\beta)p_m \qquad (5)$$

where $p_m = 1/2(p_1 + p_2)$, p_1 and p_2 are the pressures below and above the membrane respectively, and σ_0 the solubility coefficient of the gas in the polymer.

The traditional approach in the determination of the parameters of the free volume model requires a study of the diffusion in the polymer of gaseous probe molecules with different dimensions, that is the solution of the inverse diffusion problem. It should be noted that the integral free volume $V_f = v_f N$ can also be determined independently from data on the viscosity and the thermal expansion, crystallographic data, etc. At the same time, in the case of the diffusion of gases in polymers, the size distribution of the elements of the free volume is more important. This can be estimated using probe methods, which make it possible to study the behaviour in the polymer of probes of different character and dimensions, sensitive to those characteristics of the free volume which influence the diffusion of gas molecules.

Fig.2 shows the correlation between T_g and the free volume determined by the positron annihilation method[15] in the disordered regions of polymers $(v_f)_i$. Comparison of Figs.1 and 2 shows that the diffusion and permeability coefficients on the one hand, and the

free volume $(v_f)_i$ on the other, decrease in the same way with increase in the glass temperature in the highly elastic range of the polymer. This shows that the values of $(v_f)_i$ determine the diffusion coefficients of gases in rubbers in accordance with the equations of the theory of free volume. In particular, assuming that the process of gas diffusion involves chiefly the free volume in the disordered regions, and substituting $(v_f)_i$ in Eqn.(3), it is possible, from a comparison of the parameters of this equation with the dimensions of the molecules of the diffusing gases, to conclude that the geometry of the elements of the free volume in rubbers is cylindrical, in agreement with the assumed geometry of the segment of the polymer chain. It should also be noted that as T_g approaches T_m, the free volume $(v_f)_i$ decreases to a low value. This shows that the measured free volume in rubbers is sensitive to the segmental mobility.

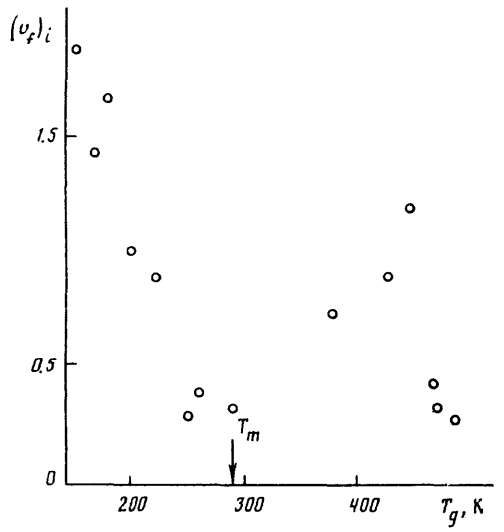


Figure 2. Correlation between the free volume $(v_f)_i$ and vitrification temperatures of polymers.[15]

At temperatures appreciably lower than T_g, the translational mobility of particles with low molecular weight is determined by the α-relaxation processes in the polymers. The small-scale† mobility in a polymer, which is often interpreted as β-transitions, is apparently appreciable close to T_g; in the highly elastic range, its contribution is small compared with that of the segmental mobility. The experimental data making it possible to estimate the role of small-scale mobility in the vitreous range will be examined below.

†The term small-scale mobility is usually employed to denote the vibrations and rotations of small groups in a polymer, which are preserved at temperatures both above and below T_g. Information on these motions in a polymer (for example the rotations of the phenyl group in polystyrene or of the methylene group of the main chain of polyvinyl chloride) can be obtained by NMR.

Among highly elastic polymers, the highest diffusion and permeability coefficients are observed for polydimethylsiloxane (PDMS) and other siloxanes differing from PDMS in the substituents on the silicon atom of the main chain (alkyl, phenyl, etc.). Polydimethylsiloxane has a lower glass temperature (150 K) than other polymers. The diffusion coefficients in it (at a temperature of 300 K) are high, and their order of magnitude is close to that of the diffusion coefficients in liquids. This is a consequence of the high flexibility of the main chain and the weak inter-chain interaction. Thus an increase in the size of the substituent (the replacement of a methyl by a phenyl group) or the introduction of a polar substituent (the nitrile group) leads to a decrease in the diffusion and permeability coefficients. It has been suggested that the elementary act in the diffusion of the molecule of a gas in a siloxane is controlled by the cooperative movement of a section of the chain containing three monomeric silicon-containing units.[16]

In spite of the high diffusion parameters of PDMS, a serious obstacle to the use of this polymer as a material for gas-separation membranes is its low selectivity with respect to many gases, and also its poor mechanical and film-forming properties. Various methods are used to overcome these disadvantages: the introduction of fillers, cross-linking, block copolymerisation, and the deposition of thin layers of PDMS on polymer supports. For example, the first gas-separation membranes were prepared from filled PDMS on a fabric support.[17] Cross-linked siloxanes are used to obtain composite membranes with a polysulphone support.[18] Non-cross-linked PDMS can be deposited on polymer supports to suppress defects or to produce thin layers with high gas-transport parameters.[19] Copolymers containing siloxane blocks will be examined in detail in section IV.

2. Vitreous Polymers

At temperatures below the vitrification temperature, the segmental mobility in a polymer disappears. From this it might have been expected that vitreous polymers would have a small free volume, and hence lower diffusion and permeability coefficients than rubbers. Since the temperature dependence of the diffusion and permeability coefficients is described by Arrhenius equations with $E_D > 0$ and $E_p > 0$, decrease in temperature leads to a decrease in P and D. In most cases, a break is observed on the Arrhenius relationships, that is the values of E_D and E_p change on passing through T_g.[6,7] At the same time, the view, which has been accepted for many years, that polymeric glasses always have lower diffusion and permeability coefficients than highly elastic polymers is not correct. In recent year, many vitreous polymers with higher diffusion and permeability coefficients than most rubbers and amorphous–crystalline polymers with low vitrification temperatures have been studied. This and other characteristics of mass transfer and sorption in vitreous polymers can be explained using the model of double sorption.[20]

Studies of the thermodynamics of sorption in a large number of vitreous polymers (see for example the paper by Paul[20] and the references therein) indicate that the sorption isotherms have the form shown in Fig.3, and are described by the equation:

$$C = k_D p + C'_H bp/(1 + bp) \qquad (6)$$

where C is the solubility, expressed in cm^3 gas (at normal temperature and pressure) per cm^3 polymer, and p the pressure, atm. The first term corresponds to the Henry isotherm (k_D is the solubility

coefficient), and the second to the Langmuir isotherm; b is the adsorption equilibrium constant, and C'_H is the adsorption capacity for the "Langmuir" fraction of the sorbed molecules. It should be borne in mind that the adsorption being considered takes place not at the gas–polymer interface but in the regions of lower density in the bulk of the vitreous polymer, that is in the elements of the non-equilibrium free volume.

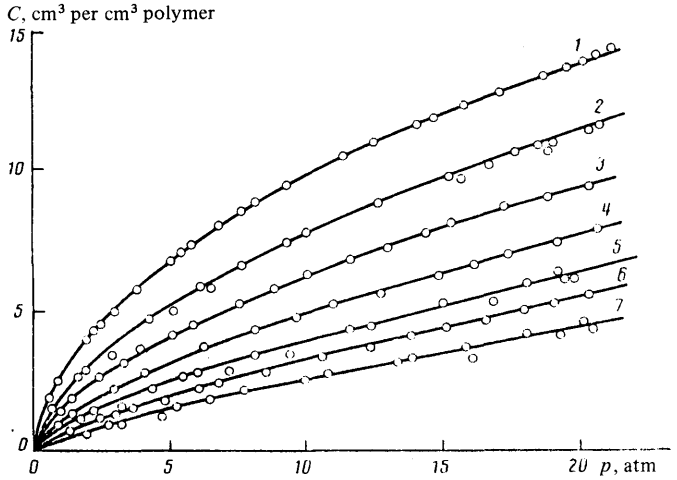


Figure 3. Sorption isotherms for carbon dioxide in polyethylene–terephthalate[21] at different temperatures K: *1*) 298, *2*) 308, *3*) 318, *4*) 328, *5*) 338, *6*) 348, *7*) 358.

The lower the temperature (in the vitreous range), the more convex the sorption isotherm towards the ordinate (see Fig.3). Since the quantity C'_H is determined as the intercept cut off on the ordinate by the asymptote approached by the sorption isotherm at high pressures (its equation is $C = C'_H + k_D p$), it follows that as T_m decreases or as the vitreous polymer moves away from its T_g, the values of C'_H increase. With increase in temperature, the curves become less convex, and at $T_m \geqslant T_g$ the isotherms become linear.

Thus the Henry isotherm describes physical solution in the polymer at temperatures both higher and lower than T_g; the second term is characteristic only of the vitreous state. At low pressures, the effective solubility coefficient is $\sigma = k_D + C'_H b$, and for highly elastic polymers, $\sigma = k_D$. This explains why the solubility coefficients are higher in polymeric glasses than in rubbers.[22] With increase in temperature, the value of σ decreases, not only because $\partial k_D/\partial T < 0$ and $\partial b/\partial T < 0$; there is a simultaneous decrease in the adsorption capacity C'_H, which reaches zero at T_g (Fig.4).

It is considered[20] that the quantity C'_H is a measure of the integral non-equilibrium free volume, which increases as the temperature $T_m < T_g$ moves into the low-temperature range. A number of data support this view. The value of C'_H at different temperatures can be determined not only from sorption data, but also from dilatometric curves.[23] This independent estimate, assuming that the density of the adsorbed gas is close to the density of its liquid phase, leads to very good agreement with the values of C'_H calculated from the sorption isotherms[21] (Fig.4).

Solution of the diffusion equation, including the two diffusion coefficients D_D and D_H for the physically dissolved and "Langmuir" fractions of the sorbate molecules respectively,[24] leads to the following expression for the observed diffusion coefficient of the gas D:

$$D = D_D \frac{1 + C'_H b/k_D}{1 + D_H C_H b/D_D k_D} \qquad (7)$$

It can readily be seen that with increase in C'_H or as the vitreous polymer moves away from its T_g, the diffusion coefficients of the gases should increase. With increase in T_g, as noted above, the diffusion coefficients of gases in polymers do in fact increase[5] (see Fig.1). This effect is evidently related to the characteristics of the thermodynamic state of polymers having high glass temperatures, since increase in T_g is accompanied by an increase in the rotational mobility of substances with low molecular weights (spin and electrochromic probes).[5] The increase in the non-equilibrium free volume in vitreous polymers whose glass temperatures are sufficiently high is also indicated by data obtained by positron annihilation[15] (Fig.2). The correlation between the activation energy of diffusion and T_g also indicates that the fraction of the free volume in polymers increases with increase in T_g.[25]

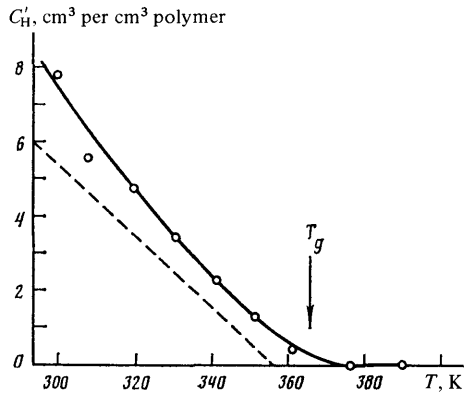


Figure 4. Temperature dependence of C'_H (for CO_2) in polyethylene–terephthalate.[21]

There arises the question of how universal are the thermodynamic relationships obtained from the model of double sorption for vitreous polymers. What is the range of change in the non-equilibrium free volume or the values of C'_H equivalent to it for different polymers? Answers to the last question are provided by the published[26] dependence of C'_H on T_g (at constant temperature) for different polymers (Fig.5). In spite of the marked differences in the chemical character of the polymers examined and the wide range of glass tem peratures, the value of C'_H is determined only by the extent to which the polymer has moved from its glass temperature. The relationshi shown in Fig.5 also applies for other sorbates (for example SO_2 [27]).

Thus the high diffusion and permeability coefficients of polymers with high glass temperatures are due to the appreciable magnitude o the non-equilibrium free volume. Physically, this means that a vitreous polymer at room temperature has the same free volume as some highly elastic polymer at a much higher temperature. The increase in the non-equilibrium free volume with decrease in the

temperature T_m in the range below T_g, that is with increase in the difference $\Delta T = T_g - T_m$, is apparently related to the fact that the decrease in the amplitude of the small-scale movements at lower values of T_m and large differences ΔT leads to the appearance in the vitreous matrix of an additional free volume, which is greater, the larger ΔT.[21,28]

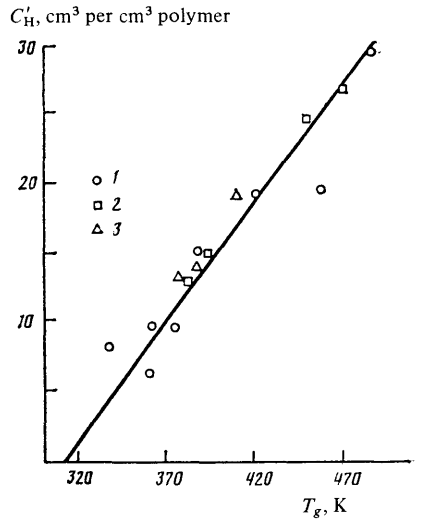


Figure 5. Correlation between the parameter C'_H for the sorption of CO_2 at 308 K and the glass temperature of polymer:[26] *1*) homopolymers, *2*) copolymers of polyphenylene oxide and polystyrene, *3*) copolymers of a polycarbonate and a polyester.

It has been suggested[29] that in the free volume, the fractions f_T and f_v corresponding to the thermal motion and the non-equilibrium character of the polymer respectively should be distinguished. Since f_T and f_v should be expected to change in opposite ways on moving away from T_g, it follows from the equation

$$D = \alpha \exp\left[-\beta(f_T + f_v)\right] \quad (8)$$

which comes from the theory of free volume, that extremal relationships may appear, for example with change in T_g by plasticising the glassy polymer. Relationships of this type have in fact been obtained for the translational and rotational mobility of substances with low molecular weight.[29–33]

Additional confirmation of the role of small-scale mobility in diffusion phenomena observed in vitreous polymers is provided by the correlation between the frequency of rotation of the small groups of the macro-chains (from NMR data with rotation of the specimen at the "magic" angle) and the diffusion coefficients of gases (H_2, CO).[32] The extremal character of the relationships for v_f is also indicated by data obtained by using electrochromic probes to study the free volume in glassy polymers.[34] These relationships are observed when T_m does not differ greatly from T_g, that is when the contribution (f_T) of the small-scale mobility to v_f becomes appreciable against the background of f_v.

Although the model of double sorption can be used to describe the mass transfer and sorption of both individual gases and their mixtures,[35] in the great majority of glassy polymers which have been studied, the phenomenological character restricts its predictive power. It is intuitively clear that the coefficients of diffusion, permeability, and gas-separation selectivity should be determined not so much by the integral free volume (C'_H) as by the size distribution of the elements of the free volume and their distribution in space, the interaction between the substance diffusing and the polymer, and the equilibrium between the two groups of sorbate molecules (physically dissolved and adsorbed).

The model cannot give this information, so that it is desirable to study diffusion and sorption in vitreous polymers by independent methods. Thus the existence of a rapidly established equilibrium between the two groups of sorbed molecules, corresponding to the Henry and Langmuir isotherms, has been demonstrated by NMR.[36] It was recently shown that by studying the thermodynamics of sorption by reverse gas chromatography it is possible to estimate the characteristic dimensions of the elements of the non-equilibrium free volume in a polymer.[37] It was found that the more closely the geometric dimensions of the sorbate molecule correspond to the dimensions of the element of the non-equilibrium free volume, the more exothermic the mixing process and the more hindered the state of the sorbed molecules. This is revealed in large negative entropy effects.

On the other hand, attempts are being made to construct a diffusion model which takes account of the energy of the inter-chain interaction and the geometric dimensions of the molecules of the diffusing substance and the substituents of the macro-chains.[38,39] It will be shown below that the available data on the diffusion and sorption properties of vitreous polymers make it possible in some cases to relate their large free volume to definite characteristics of the structure.

III. VITREOUS POLYMERS—MATERIALS FOR GAS-SEPARATION MEMBRANES

The recent increase in interest in energy-saving and ecologically clean technologies, and progress in the chemistry and technology of the treatment of polymers, led in the nineteen-seventies and eighties to the development of several types of industrial gas-separation membranes, used in various technological processes. All gas-separation membranes used in present-day practice are based on glasssy polymers.

Just as among highly elastic polymers the greatest free volume is shown by the silicon-containing polymer PDMS, among vitreous polymers the maximum values of D and P are characteristic of polymers containing Si in side groups; polyvinyltrimethylsilane (PVTMS)[40] and polytrimethylsilylpropyne (PTMSP).[41] Both PVTMS and PTMSP are amorphous high-molecular-weight polymers with high glass temperatures (170° and >200° respectively). Both polymers are readily soluble in various organic solvents, and form strong thin films. PVTMS is used to prepare a highly efficient asymmetric membrane with a diffusion layer thickness of 0.2 to 0.3 μm,[42] widely used to separate gases. The diffusion and permeability coefficients of these polymers with respect to various gases and, for comparison, the corresponding data for PDMS are given in Table 1.

It is considered that polymers in the highly elastic state are characterised by higher values of P and D than polymeric glasses. The data given in Table 2 refute these ideas. The diffusion and permeability coefficients in PVTMS are fairly high, although they are lower than the values of P and D in highly elastic PDMS. At the same time, the values of P and D for vitreous PTMSP are greater by an order of magnitude than those for PDMS.

Table 1. Permeability coefficients of organosilicon polymers and the diffusion coefficients of various gases in them.

Polymer	$10^9 P$, $cm^3.cm/cm^2.s.cmHg$				$10^7 D$, $cm^2 s^{-1}$			
	H_2	CH_4	O_2	N_2	H_2	CH_4	O_2	N_2
PDMS	65	95	60	28	430	130	160	150
PVTMS	20	1.3	4.3	1.1	180	1.8	7.6	3.6
PTMSP	700	400	400	200	—	227*	358*	255*

*Data given by Y.Ichiraku, S.A.Stern, and T.Nakagawa, J.Membrane Sci., 1987, **34**, 5.

Table 2. Permeability of the products of the polycondensation of 4,4'-hexafluoroisopropylidenediphthalic anhydride with various diamines.[44]

Diamine	$10^9 P$, $cm^3.cm/cm^2.s.cmHg$		α_{H_2/CH_4}
	H_2	CH_4	
3,5-Diaminobenzoic acid	3.4	0.012	275
1,5-Naphthylenediamine	7.8	0.072	109
1,3-Phenylenediamine	3.6	0.013	270

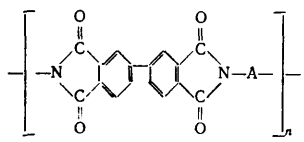
In glassy silicon-containing polymers with trimethylsilyl substituents, the appreciable free volume is probably due to the non-equilibrium state of the polymer, the large inter-chain distances, and the existence of local cavities close to the bulky substituent. This is confirmed by the relatively low density of these glassy polymers, by the results obtained by the spin probe method,[43] and by data on the thermodynamics of sorption.[37] An interesting feature is that the replacement of one methyl group by a linear alkyl group in the $Si(CH_3)_3$ groups of both glassy polymers leads to an appreciable decrease in the permeability coefficients. The long-chain alkyl group apparently fills the cavities present in the polymer, decreasing the free volume.

High diffusion coefficients are also characteristic of other polymers with bulky (non-planar) substituents: poly-4-methylpent-1-ene (PMP), poly-N-isopropylacrylamide, etc. The presence of these groups leads to relatively loose packing of the chains and to the presence of regularly arranged elements of the free volume. In particular, PMP shows an interesting characteristic: in contrast to other partly crystalline polyalkenes, its crystalline phase is characterised by an anomalously low density, lower than that of the amorphous phase. As a result, mass transfer in this polymer takes place not only through the amorphous phase but also through the crystalline phase.

Another group of vitreous polymers with high diffusion coefficients is formed by rigid-chain glassy polymers with rings in the main chain: polysulphone, polyphenylene oxide, polyimides, and cellulose acetate. The high diffusion parameters of these polymers are apparently due to weak inter-chain interactions and to steric hindrance, which prevents close packing.

The use of an aromatic polysulphone has made it possible to achieve the most impressive success in the field of industrial membrane gas-separation: the production of an asymmetric composite hollow fibre,[19] which is now used by the firm of Monsanto (USA) in apparatus for separating the gas mixtures H_2/N_2, H_2/CH_4, etc. The total number of assemblies of this kind throughout the world is much greater than 100. The coefficients of permeability and diffusion of gases in the polysulphone are lower by at least 1–2 orders of magnitude than those in the most permeable vitreous polymers, but with the thickness of the diffusion layer in the hollow fibre of ~ 0.1 μm this ensures a sufficiently high permeability with respect to hydrogen (30 litre $m^{-2} h^{-1} atm^{-1}$) with sufficiently high separation factors, for example $\alpha_{H_2/CH_4} = 37$ and $\alpha_{H_2/CO} = 23$.[19] The selectivity of the asymmetric hollow fibres, however, is only slightly lower than that of continuous films of the polysulphone, because of the thin protective covering, which "heals" defects.

Polyimides, that is the products of the polycondensation of aromatic diamines and dianhydrides, give a very high selectivity of separation of many gas mixtures. A simple and important example is provided by the polyimides obtained from the anhydride of biphenyltetracarboxylic acid:



where A is an aromatic residue. The chemical structure of polymers of this class can be varied considerably by introducing different units joining the aromatic rings, but most polymers retain high gas-transport parameters (Table 2).

The firm of Ube Industries (Japan) uses polyimides with the above structure to produce gas-separation membranes in the form of an asymmetric hollow fibre (trade mark Upilex).[45] These membranes can be used at temperatures up to 150° and pressure drops up to 140 atm, and give a separation factor of 200–250 for H_2/CH_4 mixtures.

Not only synthetic but also natural polymers can be used as material for membranes. The best examples are the cellulose esters (acetate, nitrate, ethylcellulose). The influence of hydrogen bonding decreases with increase in the degree of esterification of the cellulose. Cellulose acetate is used to produce asymmetric membranes with thin working layers with a thickness of ~ 0.1 μm,[46] used in the gas-separation equipment of the reel type which the firm of Separex (USA) offers for separating CO_2/CH_4 mixtures in the production of natural gas and in the tertiary production of petroleum. The data given below show that the gas-transport parameters of this polymer are comparable with those of polysulphone:

Gas	H_2	O_2	N_2	CH_4	CO_2	C_2H_6
$10^9 P$, $cm^3.cm/cm^2.s.cmHg$	0.35	0.068	0.023	0.014	2.0	0.0068

The H_2/CH_4 separation factor is equal to several tens of units.

IV. HETEROPHASE POLYMER MEMBRANES

The difficulty of producing polymer membranes having the required permeability, selectivity, and stability was noted above. Attempts are increasingly being made to solve this problem by using composite materials containing phases in the highly elastic and glassy states, and also the phases of low-molecular-weight solid and liquid additives.

A trend which is developing particularly actively is that associated with the production of various block copolymers, used as materials for separation membranes, into which a rigid vitreous block is introduced in addition to flexible siloxane components. This family of materials includes siloxane–carbonate,[47,48] siloxane–sulphone,[49] siloxane–arylate, siloxane–urethane, and other types of block copolymer.

In the selection of the components for the synthesis of block copolymers, particular attention is paid to the improvement of the mechanical properties, the chemical stability in the media being separated, or, finally, the selectivity of separation of the various components. In particular, the good mechanical properties of siloxane–carbonate block copolymers have made it possible to use them to produce ultrathin composite membranes with a diffusion layer thickness of 0.1–0.2 μm. The permeability coefficients of one of these membranes (MEM-079) are given below:[50]

Gas	N_2	CH_4	CO_2	H_2	H_2O
$10^9 P$, $cm^3.cm/cm^2.s.cmHg$	0.35	0.44	8.4	4.5	100

Improved mechanical and film-forming properties are also shown by siloxane–arylate block copolymers.[51] Their selectivity is determined by the selectivity of the siloxane component.

In siloxane–sulphone block copolymers,[49] since there are no easily hydrolysed Si–O–C bonds in the main chain, there is a sharp increase in the hydrolytic stability. In this respect, these block copolymers are much superior to siloxane–carbonate and siloxane–arylate block copolymers (Carbosil, Silar) and cross-linked siloxane polymers (Lestosil). The high chemical stability of polysulphones is also used in the production of other block copolymers (Seragel) which show a high selectivity in the separation of the mixtures SO_2/N_2, H_2S/CH_4, CO_2/CH_4, etc.[49]

Block copolymers in which not only the highly elastic but also the rigid (glassy) block has high gas-transport parameters might be of particular interest as selectively permeable polymers. This combination of properties has been realised in block copolymers containing PVTMS as the rigid block, and PDMS or polydienes (for example polybutadiene) as the soft (highly elastic) block.[52]

In polymers of this type, the permeability and diffusion coefficients of gases are highly sensitive to the composition and morphology of the copolymer. If the concentration of one of the components of the block copolymer is less than 20%, electron microscopy and analysis of the dependence of P and D on the copolymer composition show that it generally has a morphology of the "disperse phase–dispersion medium" (DPDM) type. At a concentration of one of the blocks equal to 50 ± 15%, phase inversion takes place, and the morphology is best described by a model of two interpenetrating networks. Since the siloxane phase has much higher values of P and D, a sharp increase in the integral diffusion and permeability coefficients is observed, and the overall composition dependence of these quantities is S-shaped. The proposed models of mass transfer in these systems (examined, in particular, in Ref.53) provide an insufficiently accurate description of the diffusion process over a wide range of compositions.

Attempts to refine the diffusion models encounter two fundamental difficulties. One difficulty is that the morphology of real heterophase block copolymers and polymer mixtures cannot always be reduced to simple structures of the DPDM type. Sometimes one of the components may form both a continuous and a disperse phase, and the latter is present in larger dispersion elements of the second component (an analogue of multiple emulsions).[54] Partial mixing of the chains at the phase interfaces and spatial non-uniformity of the membrane, for example enrichment of its surface in one of the components, are possible. As a result, different diffusion paths may be realised when different gases and vapours are transferred through these heterophase membranes.[53,55] This indicates the importance of the selection of the nature of the "diffusion probe" in the diffusion-structural analysis[56,57] of relatively complex systems of this type. In the analysis of uniform structures, the variable parameters may be the geometric dimensions of the different probes (cross-section, molar volume, etc.), whereas in the case of heterophase systems it is also necessary to vary the solubility parameter of the diffusing substance or its components, which influence the affinity of the diffusing substance and the separate phases of the polymer. At the same time, a new possibility is opened up for increasing the selectivity of gas separation using composite non-uniform membranes.

The second difficulty is that in the description of mass transfer in these membranes it is necessary to specify the local properties (coefficients of diffusion, solubility, etc.) of the individual phases. Since these are not known, it is assumed that these phases have the properties of the homopolymers. To verify the justification for this approach, it is appropriate to use probe methods. In particular, the spin probe method has shown that the diffusion coefficients of gases in the silane phase of silane–siloxane block copolymers coincide with the diffusion coefficnets in PVTMS.[53] At the same time, as shown by reverse gas chromatography[58] and spin probe[53] methods, the thermodynamic properties of the siloxane phase in copolymers differ considerably from those of PDMS.

The search for materials for separation membranes reduces to the search for polymers in which high values of P_i (and hence D_i or σ_i) for some gases are combined with low values of these parameters for other gases. In a large number of cases (He/N_2,[1] H_2/CH_4,[59] O_2/N_2 [3]) it has been shown that for most polymers, a single correlation applies: higher values of P_i correspond to a lower selectivity α_{ij}. An attractive method of overcoming this difficulty is by producing membranes in which transfer takes place through a phase in a different state of aggregation, for example in the liquid phase. The diffusion coefficients are usually greater by 2–3 orders of magnitude in liquids than in polymers. If the liquid phase filling the pores of the membrane shows selective solvent power for one of the components of the medium being separated, a highly permeable and selective membrane should be obtained. Quasi-liquid membranes of this type have been proposed for separating various gas mixtures. Some examples are given in Table 3. Attempts to use quasi-liquid membranes to separate CO, H_2S, and SO_2 from mixtures with other gases have been reported.[3]

In spite of the obvious advantages of membranes of this type, their use involves considerable technical difficulties: removal of solution from the pores of the membrane is possible; with increase in the gas pressure, the rate of transfer often does not increase, as in ordinary polymer membranes, but decreases; the effective thickness of the membranes is generally not less than 100–200 μm, whereas in polymer membranes it may be three orders of magnitude smaller; also the complex-forming reagents added to the solutions are often insufficiently stable.

Attempts are therefore still being made to give the membrane an increased selectivity with respect to the passage of certain gases without a significant lowering of the diffusion coefficients on transfer through the polymer phase.

Table 3. Characteristics of various quasi-liquid membranes.

Mixture	Diffusion medium	α_{ij}	$10^9 P_i$, $cm^3.cm/cm^2.s.cmHg$	Refs.
CO_2/CH_4	aqueous solutions of K_2CO_3 and Cs_2CO_3	—	—	[59]
CO_2/O_2	ditto	160	10	[60]
O_2/N_2	Co complexes in aqueous solutions	20—30	10^2	[3]
C_2H_4/C_2H_6	aqueous $AgNO_3$ solution	70—1000	10—10^2	[61]
Alkanes $(C_2—C_4)/CH_4$	n-decane, n-hexadecane	4—60	10^2—10^3	[62]

Specifically interacting additives may be present in the membrane as a solid solution. Thus the introduction of a number of inorganic salts (KF, KNO_3, etc.) into membranes based on mixtures of cellulose and polyethylene glycol leads to a selective increase in the permeability and solubility of CO_2, and also to selectivity of the separation of a CO_2/N_2 mixture with very little decrease in the effective diffusion coefficients of CO_2.[63] The porphyrin complex of cobalt(II), added to a polybutyl methacrylate matrix, increases both the permeability towards oxygen and α_{O_2/N_2}:[64,65]

Concentration of the complex, %	$10^9 P$, $cm^3.cm/cm^2.s.cmHg$	α_{O_2/N_2}
0	0,64	3,2
2,5	0,98	4,8
4,5	2,3	12,0

Many other types of complex interacting specifically with oxygen are known (Schiff bases, chelate complexes, haems with different structures, etc.), and their methods of synthesis and sorptive properties have been studied.[66]

If a complex-forming additive with an affinity for one of the components of the mixture being separated is not covalently bonded to the polymer, it may show a tendency to undergo phase segregation, as a result of which its efficiency decreases. Preference must be given to immobilisation of the additive on the macro-chain. There are at present few examples of studies in which an increase in selectivity and permeability has been observed as a result of the ionic, covalent, or other bonding of the complexes to the polymer matrix.[67—69] The search for membranes of this type for the concentration of oxygen from air and water is particularly intensive.

Extremely interesting possibilities for membrane gas separation are opened up by the use of polymer membranes containing low-molecular-weight liquid crystals, and membranes based on liquid-crystal polymers. Mixtures of polymers and liquid crystals with different structure and morphology show a higher permeability than the vitreous polymer matrix into which they are introduced.[70,71] These systems are characterised by a sharp inflection on the temperature dependence of the permeability coefficient with a few degrees of the temperature (T_m) of the crystal→liquid crystal transition. The values of P, for example for the C_1-C_4 hydrocarbons, increase by a factor of 100—200.[70,72,73] This increase is a consequence of the fact that at the temperature of the phase transition there is a sharp change in the solubility coefficients, but a particularly marked change in the diffusion coefficients.[74] Similar relationships were previously observed for the polyethylene—paraffin wax system;[75] an abrupt increase in the diffusion coefficients was observed in the region of the melting point of the paraffin wax.

The dependence of the permeability coefficients of C_n n-alkanes on the carbon number n is determined by the physical state of the poly-mer matrix;[22] for rubbers and partly crystalline polymers, P increases with increase in n, whereas for polymer glasses it decreases. The conversion of a system from the crystalline to the liquid-crystalline state leads to a qualitative change in the relationships, and hence in the mechanism of transfer, at temperatures below T_m, the highest permeability coefficients among C_1-C_4 n-alkanes are observed for methane, whereas above T_m they are observed for butane.[72—74] Thus the use of polymers containing added liquid crystals opens up the possibility of controlling not only the permeability but also the selectivity of membranes.

It is interesting, in particular, that in systems containing liquid crystals in the mesomorphic state, the separation factor α_{O_2/N_2} increases with increase in temperature.[76] This is an example, as yet rarely encountered, of a simultaneous increase in both the permeability and the selectivity.

Another possibility for improving the characteristics of a membrane separation process is by the effect of electrical and magnetic fields on the rate of mass transfer in the membranes. Thus the permeability coefficient with respect to n-butane increases by a factor of ~5 when an electric potential of ~700 V is applied to a membrane containing a liquid crystal, to bring about orientation of its molecules.[71]

The permeability and selectivity also depend significantly on the characteristics of the actual liquid-crystal state. Poly-γ-benzyl glutamate can form a smectic phase when obtained from a solution in benzene, and a cholesteric phase when obtained from a solution in methylene chloride. As a consequence of the lower density of packing in the cholesteric phase, the permeability coefficient with respect to benzene is six times greater.[77]

Liquid-crystal polymers should apparently have a number of advantages over mechanical mixtures of polymers and low-molecular weight liquid crystals. Studies in this direction have only just begun however. It has been established, in particular, that if the mesogenic groups (that is the groups giving the polymer its liquid-crystal properties) are in the main chain, the changes observed on passing through the temperature of the phase transition are more marked than when these groups are present in the side chains and lead to the formation of smectic liquid crystals.[76] The nature of the temperature dependence of the permeability of comb-shaped liquid-crystal polymers can be altered considerably by recrystallisation of the side chains.[78]

Almost all present-day membranes are obtained from familiar polymer materials, sometimes with slight modification. The directed synthesis of polymers for gas-separation membranes is as yet a rare exception. At the same time, accumulated knowledge of the chemical character and structure of polymers and their physical and phase states, and the understanding of the regularities and physicochemical principles of mass transfer in these materials are on the one hand providing a basis for the directed synthesis of polymers specially designed for separation membranes. On the other hand, these developments are opening up the possibility of producing membranes in the form of complex multifunctional structures.

The membranes which will be produced in the next ten years should reach a qualitatively new level: the range of gases being separated will increase, the permeability will increase by at least 1—2

orders of magnitude, and the quantitative single-stage extraction of the components of mixtures and operation under severe conditions will become possible.

While the present review was being prepared for publication, a number of papers confirming the role of the free volume in the sorption and transfer of gases in vitreous polymers were published. Maeda and Paul[79–81] have studied the influence of added plasticisers on the sorption, diffusion, and permeability of gases in polysulphone and polyphenylene oxide, and also the specific volumes of mixtures containing these polymers. It was shown that the free volume, determined as the difference $v_f = v - v_0$, where v is the specific volume, and v_0 the occupied or van der Waals volume, that is the specific volume at 0 K, provides and excellent description of the diffusion and permeability coefficients of gases in a wide range of plasticised and non-plasticised polymers. In some cases an appreciable increase in the selectivity of separation of gases α_{ij} can be achieved by changing the free volume.[82] Estimates of the characteristic dimensions of the elements of the non-equilibrium free volume in vitreous polymers by the spin probe method[43] and by reverse gas chromatography[37,83] have been confirmed by an independent determination using photochromic and fluorescent probes.[84] It was established that in polystyrene, the average volume of the elements is 260–280 Å^3, and that elements with dimensions greater than 400 Å^3 are not present, that is the size distribution is fairly narrow.

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