Noble gas transport in poly(methyl vinyl ketone) and poly(methyl vinyl ether)

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A systematic study and interpretation of the transport parameters characterizing the permeation of the noble gases, He, Ne, Ar and Kr through poly(methyl vinyl ketone) and poly(methyl vinyl ether) are presented. The results and correlations are compared with related measurements on poly(methyl acrylate) and poly(vinyl acetate). In general the measurements were conducted above the glass transition temperatures of the respective polymers. The results are interpreted in terms of the systematic variations in the physicochemical parameters of these closely related polymers. Free volume and dipole–dipole interactions appear to dominate the observed behaviour and the composite results may be explained in these terms. The size distribution of the fluctuating free volume elements and chain stiffness are also to be considered.

INTRODUCTION

Fixed gas transport in polymers above their glass transition temperatures is relatively uncomplicated. The solubilities obey Henry's law and the diffusivities are concentration independent and may be conveniently measured by the time lag method[1]. With glassy polymers both the solution and diffusion processes are complicated by dual mode sorption behaviour. Investigations into the effect of the chemical nature of the polymer on gas transport are, therefore, more conveniently conducted with polymers in the rubbery state. The experiments are further simplified if completely amorphous polymers are studied since the additional problems associated with the effect of crystallinity and morphology on the transport behaviour are avoided.

Early studies of gas transport were almost entirely concerned with elastomers which did indeed fulfill the above requirements. The elastomers were chemically rather similar and some reasonably successful correlations between various physical and chemical properties and the gas transport parameters themselves were achieved. These have been discussed recently in some detail[1]. As additional film forming polymers were developed it became clear that such correlations were rather limited. Few of the newer amorphous polymers have been studied above their glass temperatures. The most thorough study of the more polar non-elastomeric amorphous polymers was performed by Meares with poly(vinyl acetate)[2,3] (PVAc). Many years later the isomer, poly(methyl acrylate), (PMA) was investigated in these laboratories by Burgess[4] *et al.*; the four noble gases, He, Ne, Ar and Kr were studied and more recently CO_2, N_2 and O_2 have been included[5]. Evidence was presented indicating that, in spite of its lower glass temperature, the PMA chains were stiffer, more tightly packed and perhaps had a lower effective cohesive energy density than PVAc. No other systematic studies of this kind appear to have been conducted.

The present paper is concerned with a systematic study of the transport of He, Ne, Ar and Kr in two closely related polymers, poly(methyl vinyl ether) and poly(methyl vinyl ketone) above their glass temperatures. These results, coupled with those obtained with poly(vinyl acetate) and poly(methyl acrylate), should contribute to the understanding of the effects of chemical structure on gas transport and reveal correlations between the gas transport parameters and other physical properties.

EXPERIMENTAL

Materials

Poly(methyl vinyl ether) PMVE was a high molecular weight atactic material with a reduced viscosity of 2.5 at 0.1% by wt concentration in chloroform at 25°C. It was kindly supplied by Dr E. J. Vandenberg, Hercules Company, Wilmington, Delaware.

The poly(methyl vinyl ketone) PMVK was prepared by irradiating the distilled pure monomer (obtained from Polysciences, Warrington, PA) at 0.6 Mrads h^{-1} at 50°C for 30 min after sealing in an ampoule under high vacuum and thoroughly degassing. The polymer was isolated by precipitation in methanol. It was of high molecular weight with an intrinsic viscosity of 3.1 in methyl ethyl ketone at 30°C.

Helium and neon were obtained from Air Products, and argon and krypton from the Matheson Company. All the gases were greater than 99.99% pure.

Procedures

Films of PMVE were prepared by casting inside a floating glass ring on mercury from a solution in chloroform. The PMVK films were prepared similarly from a solution in acetone. The solvents were allowed to evaporate slowly and the films then dried under high vacuum for 30 days. In the case of PMVK, the films were dried and stored in the dark to avoid any photochemical degradation.

The high vacuum time lag method was used for measuring the diffusion and permeability coefficients. Details of the equipment used have recently been pub-

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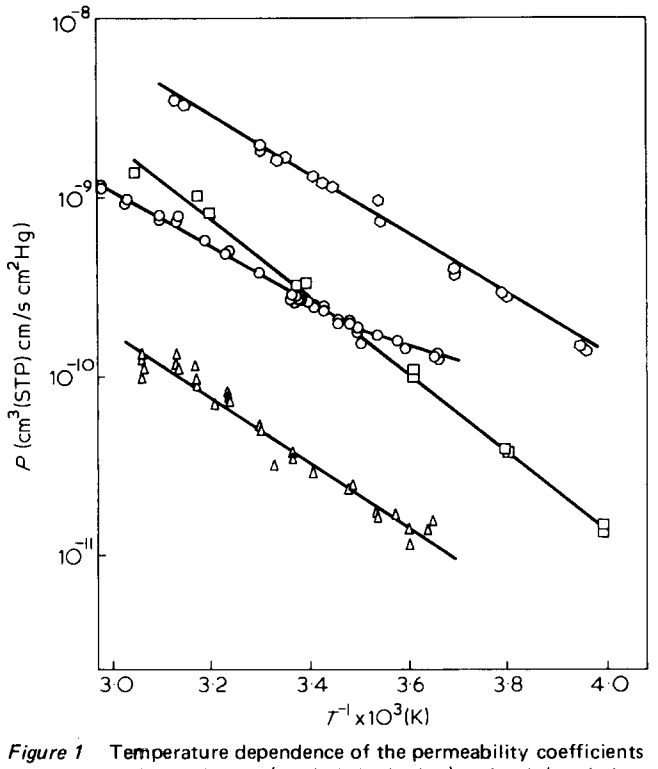

Figure 1 Temperature dependence of the permeability coefficients for helium and neon in poly(methyl vinyl ether) and poly(methyl vinyl ketone). ⬡, He–PMVE; ○, He–PMVK; □, Ne–PMVE; △, Ne–PMVK

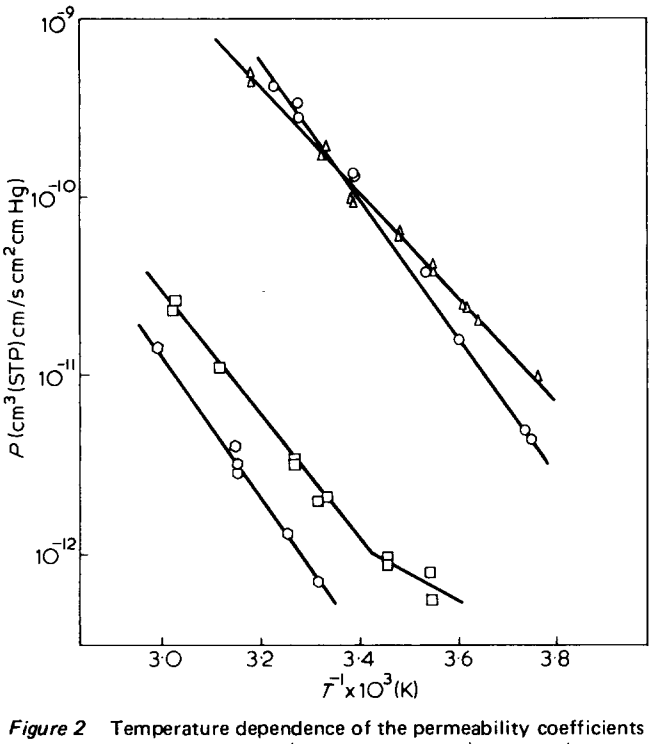

Figure 2 Temperature dependence of the permeability coefficients for argon and krypton in poly(methyl vinyl ether) and poly(methyl vinyl ketone). △, Ar–PMVE; □, Ar–PMVK; ○, Kr–PMVE; ⬡, Kr–PMVK

lished[6] and will not be repeated here. Amorphous polymers above their glass transition temperature are rather fragile and the membranes needed to be replaced from time to time.

The volume–temperature studies on PMVK were carried out by conventional glass dilatometry using mercury as the displacement fluid. Degassing was for several days at 10^{-5} torr. Further details may be found in ref 7.

RESULTS

The temperature dependence of the permeability coefficients is presented in the form of Arrhenius plots for all four noble gases in the two polymers in *Figures 1* and *2*. Arrhenius plots of the time lag diffusion coefficients are presented in *Figures 3* and *4*. A change of slope in both Arrhenius plots is suggested in the case of PMVK at 20°C, for helium and argon, which is close to the literature values of the glass transition temperature, T_g. The dilatometry results obtained with this polymer are presented in *Figure 5* and also reveal a clear T_g at 20°C. The thermal expansion coefficients in the rubbery and glassy states, α_l and α_g were found to be 4.62×10^{-4} and $1.28 \times 10^{-4}\,K^{-1}$, respectively. These lead to an $(\alpha_l - \alpha_g)\,T_g$ value of $0.098K^{-1}$, in good agreement with the numerous values reported for other polymers by Simha and Weil[8]. With neon a similar change is found with the diffusivity plot; the scatter is too great with the permeability data to show a clear break although a similar tendency can be seen. The much slower, and therefore longer, measurements with krypton resulted in frequent breakages of the films on transversing the glass temperature and no values in the glassy state were obtainable. No glass temperature has been reported in the literature within the temperature range of the measurements, −20° to +60°C, with poly(methyl vinyl ether).

The data obtained above the glass transition temperature can be used to calculate the solubilities. The least square values of all the gas transport parameters for both polymers and the four noble gases are given in *Table 1*.

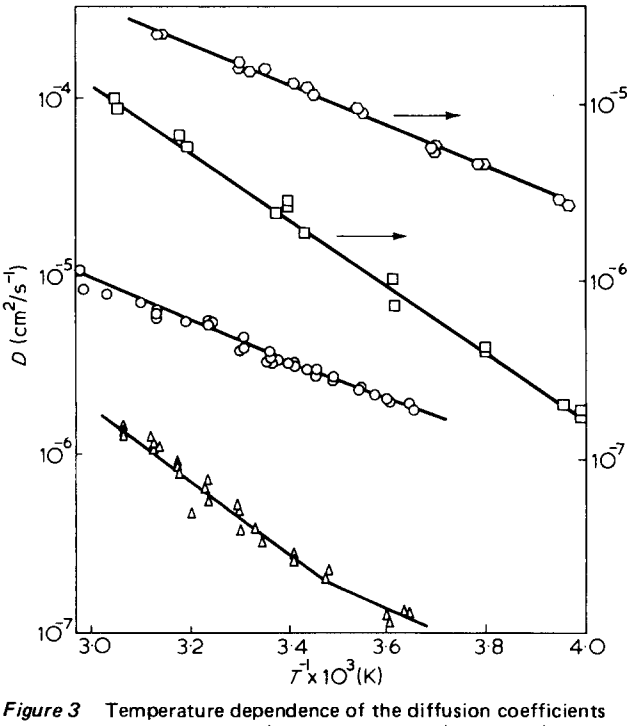

Figure 3 Temperature dependence of the diffusion coefficients for helium and neon in poly(methyl vinyl ether) and poly(methyl vinyl ketone). ⬡, He–PMVE; ○, He–PMVK; □, Ne–PMVE; △, Ne–PMVK

DISCUSSION

The permeability, diffusion, and solubility coefficients for argon at 30°C are presented in *Table 2*; the respective literature values for PVAc and PMA have also been included. PMVK has the lowest permeability and diffusivity of the four polymers and PMVE the highest. The diffusivities for helium are included in *Table 2*. Although they follow the same order they only vary by about three-fold in contrast to more than two-hundred-fold for argon. These composite results presumably reflect the increased importance of the physicochemical features of the polymers on their diffusivities as the penetrant size increases.

Although the permeabilities and diffusivities vary by 93 and 206 times respectively, the solubilities only vary by 3.4-fold. This is interesting and quite characteristic of gas transport in high polymers.

For gas transport in rubbery polymers, the permeability coefficients equal the product of the diffusion and solubility coefficients. It is more instructive, therefore, to discuss the gas transport behaviour separately in terms of solubility and diffusivity.

Diffusion behaviour

The four polymers under discussion are all amorphous, unoriented and free from crystallinity and crosslinks and were studied above their glass transition temperatures. The diffusivities and their temperature dependencies can therefore be compared with confidence with the physical properties of the polymers themselves. It is customary to try to relate gas transport behaviour with such properties as the cohesive energy densities (CED), thermal expansivities, densities, free volumes, V_f, and chain stiffness.

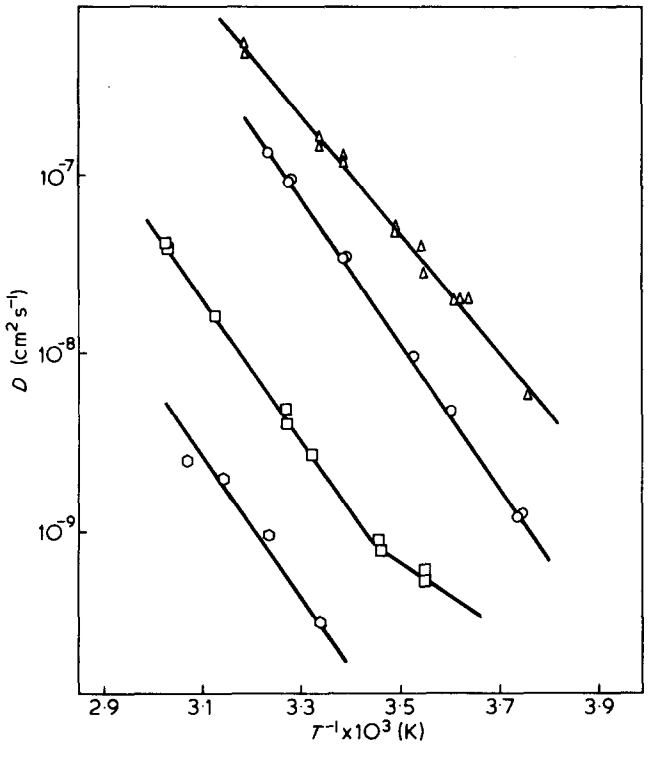

Figure 4 Temperature dependence of the diffusion coefficients for argon and krypton in poly(methyl vinyl ether) and poly(methyl vinyl ketone). △, Ar–PMVE; □, Ar–PMVK; ○, Kr–PMVE; ⬡, Kr–PMVK

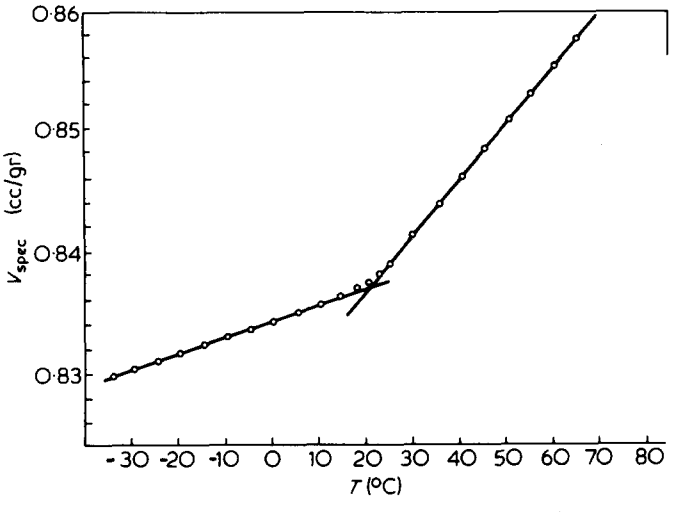

Figure 5 Specific volume *versus* temperature plot for poly(methyl vinyl ketone)

Table 2 Some transport parameters for Argon and Helium at 30°C

	Argon			Helium
	$P \times 10^{10}$	$D \times 10^{7}$	$S \times 10^{4}$	$D \times 10^{5}$
PVMK	0.024	0.032	7.38	0.48
PVAc	0.20	0.16	12.6	1.01
PMA	0.50	0.57	8.80	1.02
PVME	2.24	6.06	3.70	1.63

Table 1 Gas transport parameters for He, Ne, Ar and Kr in poly(methyl vinyl ether) and poly(methyl vinyl ketone) above their glass temperatures

Polymer	Gas	P_o	E_p	D_o	E_d	S_o	ΔH_s
Poly(methyl vinyl ether)	He	7.83×10^{-4}	7.75	0.082	5.16	9.55×10^{-3}	2.59
	Ne	8.35×10^{-4}	10.01	4.77	8.53	1.75×10^{-3}	1.48
	Ar	1.52	13.63	3.12×10^{4}	14.85	4.87×10^{-5}	−1.21
	Kr	3220.	18.13	1.30×10^{6}	18.33	2.48×10^{-3}	−0.20
Poly(methyl vinyl ketone)	He	9.87×10^{-5}	7.49	0.036	5.40	2.74×10^{-3}	2.09
	Ne	7.30×10^{-5}	8.50	2.37	9.29	3.08×10^{-5}	−0.79
	Ar	5.75	17.17	6.41×10^{4}	18.44	8.97×10^{-5}	−1.27
	Kr	602.6	20.85	4.07×10^{4}	19.41	1.48×10^{-2}	1.44

Units: P_o = cm³ (stp)/cm²/cm/s/cmHg; E_p = kcal mol^{-1}; D_o = cm² s^{-1}; E_d = kcal mol^{-1}; S_o = cm³ stp cm^{-3} polymer cmHg; ΔH_s = kcal mol^{-1}

Table 3 Physical properties and diffusivity data for Argon in four polymers

Polymer	T_g °C	*CED* cal/cc	Density g/cc	$\alpha_L \times 10^4$ °C^{-1}	*SFV* cc/g 25°C	*Ed* kcal mol^{-1}	$D \times 10^8$ cm^2 s^{-1} 25°C	at T_g
Poly(vinyl acetate)	28	109.2	1.17	6.0	0.148	16.5	1.03	1.32
Poly(methyl vinyl ketone)	20	127.5	1.22	4.6	0.107	18.4	0.20	0.11
Poly(methyl acrylate)	3	102.5	1.22	5.6	0.127	14.9	3.86	0.51
Poly(methyl vinyl ether)	−23	81.3	1.05	4.7	0.250	14.9	41.1	0.34

Table 4 'Free volume' estimates for PVAc and PMA

Polymer	D_{Ar} 25°C x 10^8	Density	$T_g\alpha$	$T_g\Delta\alpha$	WLF	Gibbs–DiMarzio	*SFV*
PVAc	1.03	1.17	0.23	0.16	0.028	0.037	0.148
PMA	3.86	1.22	0.17	0.11	0.024	0.034	0.127

Accurate values of *CED* and V_f are not known; in addition the distribution of free volume sizes and a quantitative measure of chain stiffness is not known.

A composite set of thermal, dilatometric, and transport properties for the four polymers in question is presented in *Table 3*. Free volume values for high polymers are still controversial; an excellent discussion of the difficulties of estimating free volumes has been presented by Haward[9] and by Lipatov[10]. A number of theories describe the glass transition temperature as an isofree volume state. The values of the diffusion constants have therefore been calculated at T_g, recognizing, however, that legitimate criticism of the isofree volume interpretation of T_g has been offered[9,10]. Since little extrapolation was needed, these are quite reasonable estimates and are included in *Table 2*. Lee has recently shown[11] a rather good correlation between the permeability coefficients of a large number of polymers and their specific free volumes (SFV). Of the many methods available Lee chose to use the quantity $V_T - V_0$, where V_T and V_0 are the specific volumes at temperatures T and absolute zero, respectively. V_0 can be calculated approximately from the crystal densities or that of a glass together with their coefficients of expansion as introduced by Bondi[12]. Lee combined this treatment with an estimate based on a group contribution approach described by van Krevelen and Hoftyzer[13]. The *SFV* values have been kindly computed by Lee for the four polymers and are included in *Table 3*. The computed values give lower free volumes for poly(methyl acrylate) than for poly(vinyl acetate). In a previous paper, Burgess *et al.*[4] computed the free folume fractions of these two polymers using the approaches of Simha and Boyer[14], Gibbs and DiMarzio[15], and the WLF equation[16]. All methods gave lower estimates for poly(methyl acrylate). Since the differences between these two isomers are quite subtle, it would seem that, in spite of the various approaches to estimates of free volumes, these approaches do, at least, rank them in a consistent order. The closer packing of the poly(methyl acrylate) molecules is also indicated directly by the higher density of this polymer. The actual values obtained together with the densities themselves are presented in *Table 4*.

The question of the size distribution of the fluctuating free volume elements is clearly of importance, but little is known at present about this problem. The importance of the size distribution has been discussed recently[6]. Helium presumably uses a greater fraction of the total free volume which could contribute to the comparatively low variations of the helium diffusivities as shown in *Table 2* and may reflect the importance of the size distribution of the free volume elements. A list of permeability values for helium and oxygen in 17 different polymers has recently been published. The helium values only vary by 250-fold compared with two million for oxygen[6]. Size distribution has been discussed by Frisch[17] and is a key part of the theories of Bueche[18] and Litt[19] regarding both viscosity and diffusion behaviour in high polymers.

Finally, the question of the relative chain stiffness of the polymers remains. This property is difficult to quantify; it has been suggested, however, that slope of the decrease of the specific volume with time, β, of a polymer quenched below its glass temperature would be a useful measure of chain stiffness. This approach has been discussed in a previous paper[4].

Such measurements indicated that poly(methyl acrylate) was somewhat stiffer than poly(vinyl acetate); however, the free volume is also associated with the rate of total volume relaxation in the glassy state, and the closer packing of the PMA molecules could therefore also account for the observed 14% decrease in a β compared with PVA. It appears that a better measure of the chain stiffness of polymer molecules can be obtained by a neutron scattering technique, reported by Allen[20,21] or other scattering techniques[22]. Some preliminary measurements on the four polymers, kindly performed by Allen, however, showed little motional broadening with any of the four polymers using the Harwell DIDO reactor.

Considering, first of all, only the results for PMVK and PMVE reported in this paper, the diffusion data correlate well with the physical properties of the two polymers. PMVE has a larger free volume and a lower density, lower T_g and lower cohesive energy density than PMVK. Correspondingly the diffusion coefficients for argon at 25°C and at T_g are larger and the activation energy smaller for transport in PMVE. Considering, however, all four polymers, the correspondence tends to break down. In particular the ordering of PMA and PVAc is confusing. Thd diffusivities are definitely higher with PMA and the

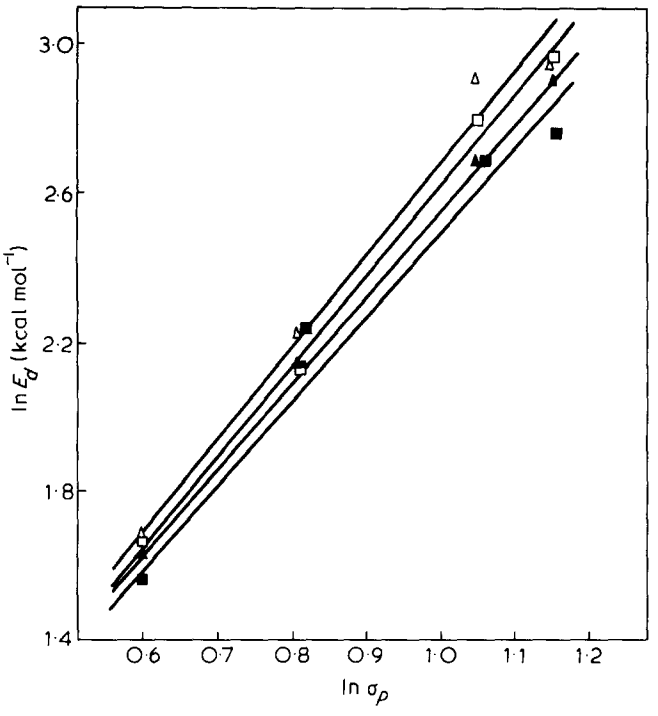

Figure 6 Logarithms of the activation energies for diffusion for the noble gases in poly(methyl vinyl ether), poly(methyl vinyl ketone), poly(vinyl acetate) and poly(methyl acrylate) *versus* their Lennard–Jones molecular diameters. ▲, PMVE; △, PMVK; □, PVAc; ■, PMA

activation energies lower. This is in spite of the fact that all the measures of free volume including the simple densities of these isomeric polymers indicate closer packing with PMA compared with PVAc.

There are two explanations which can be offered at this time. It is possible that the carbonyl groups are less shielded in PVAc than in PMA; this would diminish the effect of the comparatively powerful dipole–dipole forces in the PMA molecule. This could account for the higher activation energies for diffusion, lower diffusivities and higher glass transition temperature for PVAc compared with PMA. Such an effect should also be reflected in their cohesive energy densities. There is considerable variation in the literature values for the CED of PVAc compared with PMA and additional unequivocal measurements are needed. The average values for both polymers are given in *Table 3*. Values calculated using Small's additive method[22] have been excluded since they merely reflect the different densities of these two isomeric polymers. The mean *CED*s are 109.2 and 102.5 for PVAc and PMA, respectively, in agreement with the above reasoning. A second, somewhat related explanation, would be that PVAc has the greater chain stiffness. This question has been discussed above and in a previous paper[4]. Unfortunately there is no direct information regarding this structural feature and independent measurements such as the neutron and other scattering experiments, referred to earlier[20–22] are sorely needed.

The coefficients of expansion of the four polymers are quite similar, varying by only about 25%, no particular pattern emerges from a consideration of the individual values.

Finally two relationships found with many gas polymer systems were found to be followed with the present system. *Figure 6* shows the relationship between the Lennard–Jones diameter of the gases and the activation energies for diffusion. The range is somewhat limited and it was difficult to differentiate clearly between a first and second power dependence. In *Figure 7* log D_0 is plotted against E_d, a good linear relationship was found for all four polymers. Some fundamental reasons for this relationship are discussed in a recent review of gas transport[1].

Solubility behaviour

The solubility of the inert gases is rather independent of the nature of the polymer but highly dependent on the properties of the gas. In particular, the logarithm of the solubility varies with the boiling points, critical temperatures and the Lennard–Jones force constants of the respective gases. *Figures 8* and *9* illustrate two of these relationships for the four polymers.

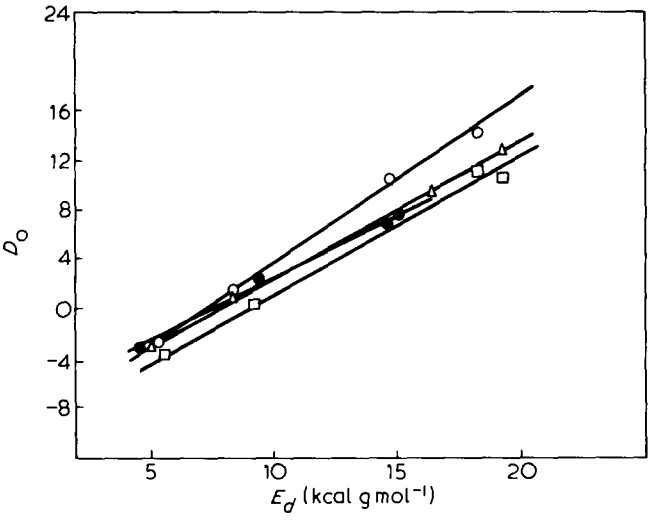

Figure 7 Logarithm of the pre-exponential factors D_0 *versus* the activation energies for diffusion for the noble gases in poly(methyl vinyl ether), poly(methyl vinyl ketone), poly(vinyl acetate) and poly(methyl acrylate). ○, PMVE; □, PMVK; △, PVAc; ●, PMA

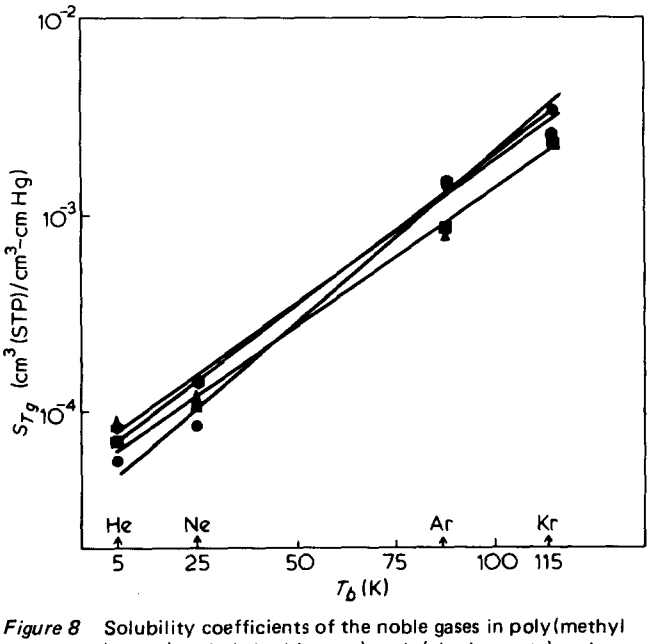

Figure 8 Solubility coefficients of the noble gases in poly(methyl vinyl ether), poly(methyl vinyl ketone), poly(vinyl acetate) and poly(methyl acrylate) at their glass transition temperatures *versus* the boiling points of the gases. ●, PMVE; ▲, PMVK; ●, PVAc; ■, PMA

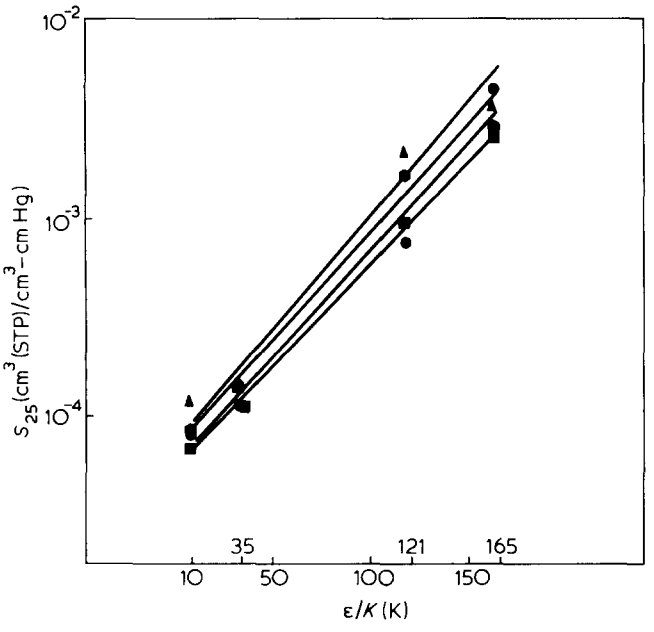

Figure 9 Solubility coefficients of the noble gases at 25°C in poly(methyl vinyl ether), poly(methyl vinyl ketone), poly(vinyl acetate) and poly(methyl acrylate) *versus* the Lennard–Jones force potential. ▲, PMVE; ■, PMVK; ○, PVAc; ●, PMA

The slopes of the boiling point correlations are 0.035 and 0.040 for PMVK and PMVE respectively. Gee has given[22] a thermodynamic interpretation of this relationship and a further discussion has recently been presented of the various correlations[1]. The theoretical slope according to Gee's treatment is equal to $10/T$ where T is measured in K, i.e., 0.034 and 0.040 for PMVK and PMVE respectively, in excellent agreement with the experimental results. The intercepts were scattered around 4.8, again in good agreement with the theoretical prediction of 4.5. The enthalpies of solution for the four polymers are given in *Table 5*. The results, although confounded with experimental error, are consistent with those found with most rubbery polymers. The noble gases in general, have small, positive enthalpies of solution in each polymer.

Table 5 Enthalpies of solution of the noble gases in four polymers

Polymer	ΔH_S kcal mol^{-1}			
	He	Ne	Ar	Kr
Poly(vinyl acetate)	2.11	1.05	−1.88	−1.20
Poly(methyl vinyl ketone)	2.10	−0.80	−1.25	1.44
Poly(methyl acrylate)	2.01	−0.85	1.20	1.27
Poly(methyl vinyl ether)	2.60	1.50	−1.21	−0.19

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