

Comparison of Gas Permeation in Vinyl and Vinylidene Polymers

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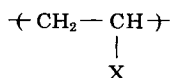
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SYNOPSIS

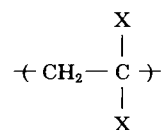
The gas transport properties of several simple vinyl and vinylidene polymers are compared to examine the effect of pendant group type (H, CH₃, F, Cl) and symmetry of placement. The literature contains extensive information about these polymers, which has been critically reviewed to obtain consistent data for interpretation of the effect of structure on gas permeability. The gas transport data available for many of these polymers are quite variable because of differences in additives, thermal history, and crystallinity. The values used here are from studies where the physical properties of the film were reported along with the transport data. The appropriate data were not available for poly(vinyl fluoride) or poly(vinylidene chloride). For poly(vinyl fluoride), permeability measurements and thermal analysis were done to supply this information. Results for poly(vinylidene chloride) were obtained by extrapolation of copolymer permeation properties. Estimates of the permeability of oxygen in the amorphous phase of each polymer are discussed in terms of the estimated fractional free volume of that phase. In this way, the intrinsic effects of molecular structure on gas permeation exclusive of crystallinity effects have been evaluated.

INTRODUCTION

Because of the importance of polymers as barrier materials and as membranes, there has been much interest in the effects of structure on their permeability coefficients for gases and the related solubility and diffusivity factors.¹⁻⁵ Gas transport properties are intimately related to chain geometry, flexibility, packing, and interactions with other chains or with the penetrant. It is, in general, very difficult to separate the effects of each issue from all the others; however, understanding can be increased by comparing the effects of systematic variations in structure within a limited series of materials as many previous studies have shown.¹⁻⁸ Our purpose here is to examine the structurally simple series of vinyl



and vinylidene



polymers where X is CH₃ or halogens. Of course, polyethylene with X = H is a degenerate member of both the vinyl and the vinylidene series (see Table I). The comparison of the halogen-containing members is limited to X = F and Cl since the polymers where X = Br are thermally unstable^{9,10} and attempts to obtain transport information were not successful.

The literature contains extensive information about the polymers shown in Table I including varying amounts of data on gas permeability.¹¹⁻⁵⁴ The objective here was to critically select from the available literature information that would allow some interpretation of the effect of the structure of the polymers in Table I on their gas permeability. It was necessary to supplement this with some new information.

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Table I The Structure, Glass Transition, and Melting Temperatures of the Vinyl and Vinylidene Polymer Series

X ↓	Vinyl — [CH ₂ —CHX] —			Vinylidene — [CH ₂ —CX ₂] —		
	Name	T _g (°C)	T _m (°C)	Name	T _g (°C)	T _m (°C)
H	Polyethylene ^a	-125 (Ref. 11)	137-141 (Ref. 11)	Polyethylene ^a	-125 (Ref. 11)	137-141 (Ref. 11)
CH ₃	Polypropylene	-10 (Ref. 11)	161-163 (Ref. 21)	Polyisobutylene	-71 (Ref. 22)	—
F	Poly(vinyl fluoride)	41 ^b	196 ^b	Poly(vinylidene fluoride)	-40 (Ref. 31)	160 (Ref. 31)
Cl	Poly(vinyl chloride)	81 (Ref. 11)	192 (Refs. 36, 38)	Poly(vinylidene chloride)	-18 (Ref. 41)	200 (Ref. 42)

^a Polyethylene can be viewed as a degenerate number of either the vinyl series or the vinylidene series.

^b This work.

These polymers have a wide range of glass transition temperatures (T_g) as can be seen in Table I. The increase in going from top to bottom from either series in Table I reflects the combined effects of the size of X and the increase in cohesion caused by polarity. The unsymmetric vinyl polymers have a higher T_g than do the symmetrical vinylidene polymers for every X, a phenomenon documented and correlated by Boyer⁵⁵ and Beaman.⁵⁶

The ability to crystallize, in general, is favored by geometrical regularity of molecular structure and by strong cohesive forces. Thus, the symmetrical polymers considered here, polyethylene, poly(vinylidene chloride), poly(vinylidene fluoride), are crystalline with the melting temperatures shown in Table I. Because of low cohesion and its bulky methyl groups, polyisobutylene does not crystallize, except under extreme conditions, even though it is symmetrical. For the unsymmetrical vinyl polymers, tacticity strongly affects their tendency for crystallization. Poly(vinyl chloride) and poly(vinyl fluoride) are made commercially by free radical polymerization and are atactic. Atactic poly(vinyl chloride) tends to be less crystalline than is atactic poly(vinyl fluoride) since the chlorine atom is larger and, thus, interferes more with the ability to crystallize than does the fluorine atom. Atactic polypropylene is generally amorphous, yet isotactic polypropylene, made by coordination polymerization, is more regular and is quite crystalline.

The gas permeability data available for many of the polymers in Table I are quite variable because of differences in additives, thermal history, crystallinity, etc. The values used here are from studies where the physical properties of the film, such as degree of crystallinity, purity, and density, were reported along with the transport data. The appropriate data were not directly available for poly(vinyl fluoride) and poly(vinylidene chloride). For poly(vinyl fluoride), the permeability measurements and thermal analysis was done in our laboratories. For poly(vinylidene chloride), copolymer permeation properties were extrapolated as described below. The permeability of oxygen in the amorphous phase of each polymer is estimated and discussed in terms of to the estimated fractional free volume of that phase.

BACKGROUND

Penetrant molecules are generally thought to be insoluble in polymer crystallites and, therefore, are unable to diffuse through them.^{12-14,57,58} Thus, gas permeation in semicrystalline polymers is confined

to the amorphous regions between crystallites. The crystallites reduce the permeability by decreasing the volume of polymer available for penetrant solution and by constraining the diffusion along irregular tortuous paths between the crystallites. The reduction in solubility, S , is directly proportional to the volume fraction of crystalline phase⁵⁹

$$S = S_a(1 - \Phi_c) \quad (1)$$

where S_a is the solubility coefficient for the completely amorphous material and Φ_c is the crystalline volume fraction. The decrease in diffusivity is a complex function of the crystallite shape and size distribution as well as their volume concentration.¹⁴ However, as an approximation, the effective diffusivity, D , can be related to the diffusion coefficient in the amorphous phase, D_a , by the simple relation

$$D = D_a(1 - \Phi_c) \quad (2)$$

The permeability coefficient, P , is the product of the effective diffusion, D , and solubility, S coefficients; therefore, combining Eqs. (1) and (2) gives

$$P = P_a(1 - \Phi_c)^2 \quad (3)$$

where P_a is the product of S_a and D_a . In this manner, the permeability coefficient for the completely amorphous polymer can be approximated.

The diffusion of a gas molecule through a polymer depends mainly on the nature of the gas and of the polymer. The effects various molecular factors have on permeability manifest themselves to a certain approximation in terms of a free-volume concept.⁶⁰⁻⁶² The fractional free volume (FFV) of a polymer may be defined as

$$FFV = \frac{V - V_0}{V} \quad (4)$$

where V is the measured specific volume and V_0 is the volume of the polymer at 0 K that may be taken to represent the occupied volume. Group contribution methods⁶³⁻⁶⁵ can be used to estimate V_0 , and previous work⁶² has shown that the Bondi method gives the best statistical correlation with gas permeation.

MATERIALS AND PROCEDURES

Gas transport measurements and film characterization were done for poly(vinyl fluoride). A sam-

ple of poly(vinyl fluoride) film obtained from DuPont (Wilmington, DE) designated as Tedlar TTR10SG30 and was 1 mil in thickness.

Pure gas permeability measurements at 35°C were made for six gases using the previously described techniques of this laboratory^{66,67} where essentially zero pressure was maintained on the downstream and the increase in pressure with time was measured by a sensitive pressure transducer and recorded.

Differential scanning calorimetry (DSC) evaluations were made using a Perkin-Elmer DSC-7 at a heating rate of 20°C/min. The sample was scanned twice consecutively, and the glass transition and melting temperatures reported were taken as the midpoint of the transitions from the second scan. The degree of crystallinity was calculated from the heat of fusion determined from the area under the melting peak of the first scan.

RESULTS AND DISCUSSION

Permeability coefficients at 35°C for the vinyl and vinylidene polymers are shown in Table II. The values shown for polyethylene, polypropylene, and polyisobutylene are what we consider to be the most commonly accepted values. Permeability coefficients for poly(vinyl chloride) and poly(vinylidene fluoride) were previously measured in our laboratories, whereas those for poly(vinyl fluoride) were determined specifically for this study. In these cases, the polymer sample was fully characterized, thereby resolving questions concerning purity and crystallinity. Permeability data for poly(vinylidene chloride) were determined by extrapolating data from copolymer permeability vs. composition plots, as described below. In the following paragraphs, each

polymer in the series and the sources of available data are discussed. The effects of the various molecular factors on permeability will be examined in terms of free-volume theory, and for this analysis, the amorphous density of each polymer is needed. To this end, the value selected and its origin are discussed.

Polyethylene

The gas transport properties of various polyethylene samples have been reported¹²⁻¹⁹ and show the effect of crystallinity on gas sorption and transport.^{12,13,16} The permeability coefficients for polyethylene in Table II are taken from the study by Michaels and Bixler¹⁴ for a 43% crystalline sample with a density of 0.914 g/cm³. The values have been corrected from 25°C to 35°C using the permeation activation energies reported in the same work. The density of completely amorphous polyethylene is 0.854 g/cm³.^{12,14}

Polypropylene

Commercial polypropylene is isotactic and crystalline. In the work by Meyers et al., the permeability coefficients of nitrogen, oxygen, and carbon dioxide were measured at 30°C for a 50% crystalline sample of density 0.907 g/cm³.¹⁹ The values recorded in Table II have been corrected to 35°C using the activation energies reported in the same work. The amorphous density of polypropylene is 0.856 g/cm³.²⁰

Polyisobutylene

Polyisobutylene is an amorphous elastomer and has limited applicability as a homopolymer. It is more commonly used with a small amount of isoprene

Table II Permeability Coefficients at 35°C

Polymer	Permeability ^a						Reference
	N ₂	O ₂	CH ₄	H ₂	He	CO ₂	
Polyethylene	1.9	5.1	5.4	—	7.8	21.0	14
Polypropylene	0.63	3.1	—	—	—	11.8	19
Polyisobutylene	0.58	2.1	1.4	10.9	11.2	8.7	23
Poly(vinyl fluoride)	0.009	0.04	0.01	0.54	1.3	0.27	^b
Poly(vinylidene fluoride)	0.022	0.083	0.02	0.54	1.7	0.52	31
Poly(vinyl chloride)	0.007	0.094	0.0085	—	2.9	0.18	37, 38
Poly(vinylidene chloride)	—	0.0005	—	—	—	—	^b

^a Units: 10⁻¹⁰ cm³(STP) cm/cm² s cmHg.

^b See text.

added, forming the copolymer butyl rubber. Permeability coefficients at 35°C for pure polyisobutylene were measured by van Amerongen.²³ The density of high molecular weight polyisobutylene is 0.910 g/cm³.²⁴

Poly(Vinyl Fluoride)

Permeability data for poly(vinyl fluoride), or Tedlar, are primarily available from the industrial brochures of DuPont.²⁵ The physical properties of poly(vinyl fluoride) including a small amount of permeability data, have been reported.^{26,27} A sample of poly(vinyl fluoride) was obtained from DuPont, and permeability coefficients for six gases were measured in our laboratories. The values obtained are shown in Table II, and the coefficients for hydrogen, helium, and oxygen agree well (after extrapolation to 35°C) with those reported by DuPont.²⁵ The values measured for nitrogen and carbon dioxide are a factor of 2.2 and 2.4 times higher than those reported by DuPont.

The crystalline content of the film was determined in our laboratory to be 38% from the heat of fusion measured by differential scanning calorimetry using the reported value of 164.8 J/g for the heat of fusion for the 100% crystalline material.²⁸ A value for the amorphous density of poly(vinyl fluoride) is not available; however, it is possible to make an es-

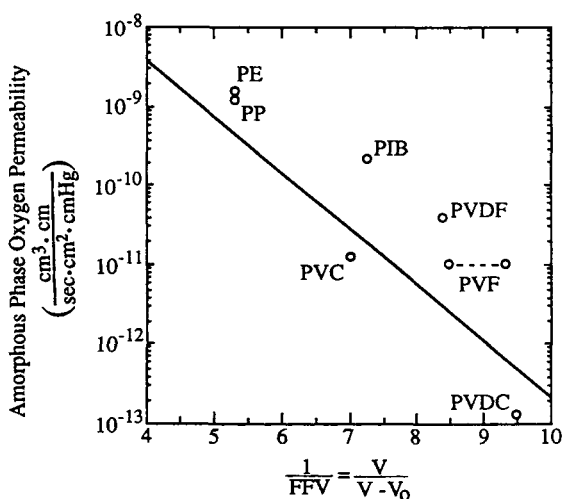


Figure 1 Amorphous phase oxygen permeability at 35°C vs. reciprocal fractional free volume of amorphous phase for the vinyl and vinylidene polymers. The solid line represents a general correlation for a number of amorphous, glassy polymers. The two points for poly(vinyl fluoride) (PVF) were calculated for sample densities of 1.38 g/cm³ (left) and 1.39 g/cm³ (right).

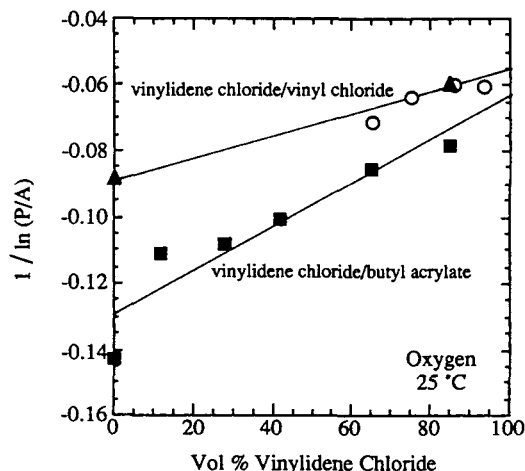


Figure 2 Oxygen permeability of vinylidene chloride copolymers plotted in the manner suggested by eq. 5. Comonomer = vinyl chloride (\blacktriangle , \circ), butyl acrylate (\blacksquare).

timate¹³ knowing that the density of the crystal is 1.44 g/cm³ (Ref. 29) and the crystalline fraction is 0.38. Two values for the density of poly(vinyl fluoride) have been reported: 1.39 g/cm³ (Ref. 30) and 1.38 g/cm³.^{27,29} The amorphous densities calculated from these sample densities are 1.36 g/cm³ and 1.34 g/cm³, respectively. Free-volume calculations using both values are shown in Figure 1.

Poly(Vinylidene Fluoride)

Poly(vinylidene fluoride) is a good barrier material with excellent chemical resistance and has been the subject of several characterization studies.³¹⁻³⁴ In particular, the work of El-Hibri and Paul focused on the gas transport properties³¹ of a 6 mil film obtained from Pennwalt Corporation (Philadelphia, PA) that was 54% crystalline. The permeability coefficients from this study are reported in Table II. The density of amorphous poly(vinylidene fluoride) is 1.67 g/cm³.³⁵

Poly(Vinyl Chloride)

The gas sorption and transport properties of unmodified poly(vinyl chloride) have been reported by Tikhomirov et al.³⁷ and by our laboratory.³⁸ The permeability coefficients reported in Table II are from the work of El-Hibri on a film containing no additives except for 2% of a tin stabilizer. Thermal analysis indicated a crystalline fraction of approximately 10%, which is common for commercial poly(vinyl chloride).³⁹ The amorphous density of commercial poly(vinyl chloride) is 1.41 g/cm³.⁴⁰

Table III Volumetric Characteristics for the Vinyl and Vinylidene Polymer Series

X ↓	Vinyl — [CH ₂ —CHX]—				Vinylidene — [CH ₂ —CX ₂]—			
	Name	Density ^a (g/cm ³)	V _w ^b (cm ³ /mol)	FFV ^c	Name	Density ^a (g/cm ³)	V _w ^b (cm ³ /mol)	FFV ^c
H	Polyethylene	0.854 (Ref. 14)	20.46	0.189	Polyethylene	0.854 (Ref. 14)	20.46	0.189
CH ₃	Polypropylene	0.856 (Ref. 20)	30.68	0.189	Polyisobutylene	0.910 (Ref. 24)	40.90	0.138
F	Poly(vinyl fluoride)	1.34 ^d	23.23	0.118 ^e	Poly(vinylidene fluoride)	1.67 (Ref. 35)	25.56	0.119
Cl	Poly(vinyl chloride)	1.41 (Ref. 40)	29.23	0.142	Poly(vinylidene chloride)	1.78 (Refs. 51, 53)	38.03	0.106

^a Density of the amorphous fraction.

^b Van der Waals volume⁶⁸ for repeat unit.

^c Fractional free volume defined by Eq. (4).

^d Based on sample density of 1.38 g/cm³. FFV calculated for sample density of 1.39 g/cm³ is 0.107.

^e Estimated knowing the crystalline density and fraction as described in text.

Table IV Summary of Crystallinity and Oxygen Permeability Coefficients for the Vinyl and Vinylidene Polymer Series

X ↓	Vinyl — [CH ₂ —CHX]—				Vinylidene — [CH ₂ —CX ₂]—			
	Name	φ _c ^a	(P _{O₂}) ^b	(P _{O₂}) ^c	Name	φ _c ^a	(P _{O₂}) ^b	(P _{O₂}) ^c
H	Polyethylene	0.43 (Ref. 14)	5.1	15.7	Polyethylene	0.57 (Ref. 14)	5.1	15.7
CH ₃	Polypropylene	0.59 (Ref. 19)	3.1	12.4	Polyisobutylene	0	2.1	2.1
F	Poly(vinyl fluoride)	0.38 ^d	0.04	0.10	Poly(vinylidene fluoride)	0.54 (Ref. 31)	0.083	0.39
Cl	Poly(vinyl chloride)	0.10 (Ref. 39)	0.094 (Ref. 37)	0.12	Poly(vinylidene chloride)	0.40 (Ref. 49)	0.0005	0.0013

^a Crystalline fraction. Information obtained from the references indicated.

^b Oxygen permeability at 35°C. Units: 10⁻¹⁰ cm³(STP) cm/cm² s cmHg.

^c Oxygen permeability of the amorphous phase estimated from information in ^a and ^b using Eq. (3).

^d This work.

Poly(Vinylidene Chloride)

Poly(vinylidene chloride) is a semicrystalline polymer with an extremely low permeability to gases and vapors. Poly(vinylidene chloride) is rarely used or studied as a homopolymer because it is extremely difficult to process or to dissolve. However, a variety of monomers can be polymerized with vinylidene chloride, and the resulting commercial copolymers are known by the tradename Saran.^{43,44} The good barrier properties of Saran has led to a number of studies on water and gas transmission rates.⁴⁴⁻⁵¹ Permeability data for the homopolymer are not available; however, it can be approximated from the copolymer data in the following manner.

Paul⁶⁸ has shown from a simple free-volume model that the permeability, P , of multicomponent polymer systems can be expected to follow the mixing rule

$$\ln \frac{P}{A} = \left(\frac{\phi_1}{\ln(P_1/A)} + \frac{\phi_2}{\ln(P_2/A)} \right)^{-1} \quad (5)$$

where ϕ_i is the volume fraction of component i and P_i is its permeability coefficient. The parameter A is a constant for a particular gas. A plot of $[1/\ln(P/A)]$ vs. comonomer volume fraction ought to give a line that can be extrapolated to give the permeability coefficients of the components.

Several works by Delassus provide oxygen gas transport information on the copolymers of vinylidene chloride with vinyl chloride^{49,50} and with butyl acrylate.⁵¹ The oxygen permeability data from these studies are plotted in Figure 2 as $[1/\ln(P/A)]$ vs. vinylidene chloride volume fraction, where a value of $7.9 \times 10^{-7} \text{ cm}^3 \text{ cm/s cm}^2 \text{ cmHg}$ was used for the parameter A .⁶⁸ As described above, the permeability coefficient for pure poly(vinylidene chloride) is approximated by extrapolation of the lines to 100% vinylidene chloride. The upper line in Figure 1 corresponds to the vinyl chloride–vinylidene chloride system,⁴⁹ and it extrapolates to an oxygen permeability of approximately $2.0 \times 10^{-14} \text{ cm}^3 \text{ cm/s cm}^2 \text{ cmHg}$ after further extrapolation from 25°C to 35°C using the oxygen activation energy of 18.3 kcal/mol reported in the same work.⁴⁹ The oxygen permeability obtained by extrapolating the lower line for the butyl acrylate–vinylidene chloride system⁵¹ gives $3.5 \times 10^{-13} \text{ cm}^3 \text{ cm/s cm}^2 \text{ cmHg}$, after correction to 35°C. There is some uncertainty in each of these extrapolations due to small amounts of additives. More recently, the oxygen permeabilities of four vi-

nylidene chloride/vinyl chloride copolymers were reported.⁵⁰ The open data points in Figure 2 correspond to these data that fall along the upper line previously discussed. These data extrapolate to an oxygen permeability coefficient of $4.7 \times 10^{-14} \text{ cm}^3 \text{ cm/s cm}^2 \text{ cmHg}$ (corrected to 35°C), in good agreement with the extrapolation based on the upper line. We have taken the value $4.7 \times 10^{-14} \text{ cm}^3 \text{ cm/s cm}^2 \text{ cmHg}$ to represent the oxygen permeability coefficient for the poly(vinylidene chloride) homopolymer. The crystalline content of the vinylidene chloride/vinyl chloride copolymer was 40%.⁴⁹ Okuda⁵² has reported a value of 43% for the crystalline fraction of poly(vinylidene chloride). These values are close, and we have chosen to use 40% for further calculations.

The amorphous density of poly(vinylidene chloride) has been reported to be 1.775 g/cm^3 (Refs. 51 and 53) and 1.757 g/cm^3 (Ref. 54) and the former is used in subsequent calculations.

Table III summarizes the amorphous phase densities for each of the polymers. The fractional free volume was calculated according to Eq. (4) using this amorphous density and the relation⁶⁴

$$V_0 = 1.3V_w \quad (6)$$

where V_w is the van der Waals volume obtained by a group contribution method.^{63,69} In general, the estimated amorphous phase free volume tends to decrease within each series from top to bottom in Table III. Poly(vinyl fluoride) and poly(vinyl chloride) are an exception to this; however, it should be noted that the estimate for the amorphous density of poly(vinyl fluoride) is rather crude. Polyethylene and polypropylene have about the same fractional free volume. Also, there is a rather consistent trend for the fractional free volume to be lower for the vinylidene polymers than for the corresponding vinyl polymers. Again poly(vinyl fluoride) is something of an exception since it has been estimated to have a slightly lower free volume than does poly(vinylidene fluoride).

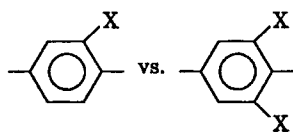
Effect of Structure on Permeability

For simplicity, this discussion will be restricted to oxygen permeability. This choice is logical because there is more interest in this gas and, therefore, more complete and better data for it. For the most part, the same trends will apply to other gases but not

for water vapor. Table IV summarizes the oxygen permeability results obtained from the sources described earlier. In addition, there is an estimate of the permeability of the amorphous phase obtained from Eq. (3). Qualitatively, the trends are the same whether we compare the actual permeability or the estimated ones for the amorphous phase. However, for quantitative comparison, it may be informative to use the latter since the crystallinity effect does vary widely among these polymers.

In general, the gas permeability decreases from top to bottom and from left to right in Table IV, that is, in general, polarity and symmetry tend to lower the permeability. Again, poly(vinyl fluoride) is an exception to these trends since it is a better barrier than are both poly(vinyl chloride) and poly(vinylidene fluoride). This is an interesting point for which there is no readily apparent explanation.

The effect of symmetry noted here has an interesting counter example in the case of rigid chain glassy polymers. In other work,^{5,70} we showed that unsymmetrical substitutions on rings in the backbone lead to lower permeability than symmetrical substitution, i.e.,



Similarly, symmetrical *para*-connected backbone rings lead to higher permeability than do unsymmetrical meta connected rings.⁷⁰⁻⁷²

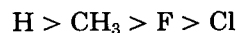
The measured density of a polymer reflects the diverse effects of pendant group size, polarity, and symmetry. The simple free volume estimated from the density via Eq. (4) has proven useful for correlating permeability data for a number of amorphous, glassy polymers.⁶⁰⁻⁶² To apply this approach for dealing with permeability-structure relationships to the current series of polymers presents some difficulties. A major one is knowing the actual permeability and density of the amorphous phase with accuracy. Another involves comparing polymers that are well above their glass transitions with glassy polymers. Nevertheless, Figure 1 shows an attempt to do this. The solid line is the correlation that was found for a wide range of totally amorphous, glassy polymers.⁶² Given all the limitations mentioned, the general trend for the vinyl and vinylidene series is remarkable. For example, this treatment seems to

account for the intrinsic differences in barrier properties of polyisobutylene compared to amorphous polyethylene and polypropylene. It is interesting to note that all the hydrocarbon polymers and those containing fluorine lie above the solid line in Figure 1, whereas both polymers containing chlorine fall below this line. All these polymers are above their glass transition temperatures at 35°C except for poly(vinyl chloride) and poly(vinyl fluoride). One might make something of a case for rubbery polymers having a higher permeability than do glassy polymers at the same fractional free volume, although the evidence for this is rather limited. Because of the significant deviation of the chlorine-containing polymers from the trends of the rest, we may conclude that either they are better barriers than the fractional free-volume approach would suggest or there is some systematic error in the group contribution to occupied volume for chlorine atoms. The latter possibility deserves further investigation before any more far-reaching conclusion is seriously considered.

For poly(vinyl fluoride), Figure 1 shows two fractional free-volume values calculated from the previously discussed different densities reported for the semicrystalline material. This serves to illustrate the sensitivity to the uncertainty. Even with the crude estimate of volumetric information for this polymer, it seems to fall in line with the other polymers in this series except, of course, for those involving chlorine.

CONCLUSIONS

For the vinyl and vinylidene polymer series considered here, we have attempted to evaluate the intrinsic effects of molecular structure on gas permeation exclusive of crystallinity effects. Except for poly(vinyl fluoride), permeability to gases changes with X in the order



with permeability values being lower for the symmetrical vinylidene series relative to the unsymmetrical vinyl series. From a simple structural point of view, it is not clear why poly(vinyl fluoride) does not fit this pattern. Estimates of fractional free volume, even though crude, do seem to account for the permeability differences observed. The two chlorine containing polymers are an exception to this as their

permeability is lower than the fractional free volume would predict.

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