Gas sorption and transport in semicrystalline poly(4-methyl-1-pentene)

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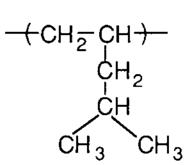
The solubility of CO_2 and CH_4 plus permeability coefficients for these and other gases were measured for a series of poly(4-methyl-1-pentene) polymers with crystallinity levels ranging from 20% to 75%. The crystallinity was varied through thermal treatment and by addition of a comonomer that permitted thermally-induced crosslinking. An extrapolation, assuming a two-phase model, of the sorption results to 100% crystallinity indicates a finite solubility for CO_2 and CH_4 in the crystal (about 25–30% of the solubility for the amorphous phase). Regression analysis of the permeation data using a two-phase transport model indicated that diffusion occurs at finite rates in the crystal. This is contrary to the usual situation for polymers like polyethylene but is consistent with the unusual fact that the density of the poly(4-methyl-1-pentene) crystal is slightly less than that of the amorphous phase. The diffusion rate in the crystal appears to become nil as the dimensions of the gas molecules exceed the estimated gap sizes between chains in the crystal.

(Keywords: gas transport; solubility; poly(4-methyl-1-pentene))

INTRODUCTION

It is generally accepted that sorption and transport of gases and vapours occur exclusively in the amorphous phase of semicrystalline polymers and that crystallites act as impermeable barriers to the diffusing molecules. One of the earliest indications of any effect of crystallinity was van Amerongen's 1947 report[1] that the crystallization of gutta-percha produced a marked decrease in gas permeability. Comparable results were observed by Doty *et al.*[2] while investigating water vapour permeation in natural rubber. However, studies designed primarily to isolate the effects of crystallites were not carried out until the late 1950s[3–6]. Meyers *et al.*[3] first suggested that small molecules dissolved only in the amorphous regions based on the sorption of methyl bromide vapours in polyethylenes of different levels of crystallinity. Lasoski and Cobbs[4] measured water vapour permeability as a function of the crystalline content of poly(ethylene terephthalate), nylon 610 and polyethylene, and proposed that permeability was proportional to the square of the amorphous fraction of the polymer. At about the same time, others[3,7] attempted to develop equations to predict permeation in semicrystalline materials by assuming the crystallites to be a dispersion of impermeable spheres. Starting in 1959, Michaels and coworkers[8–13] published an extensive series of investigations that analysed the relationships between polymer morphology and the gas transport process. The results and conclusions from the above mentioned studies provide the basis for the most widely accepted physical picture of transport in semicrystalline materials used today, i.e. the concept that the crystallites are impenetrable barriers which may even impede diffusion in the amorphous phase.

In the polymers considered above, the crystalline phase is substantially more dense than the amorphous phase. For example, the crystalline and amorphous densities of polyethylene differ by about 15%[14], so it is not surprising that small molecules find the crystals effectively impenetrable relative to the less dense amorphous regions. On the other hand, poly(4-methyl-1-pentene) (PMP) is a semicrystalline polymer with a very low density due to inefficient packing of the bulky pendant group. PMP has the following structure:



It also displays the unusual feature of a crystal density slightly lower than that of the amorphous phase at room temperature. Many density values have been reported in the literature for poly(4-methyl-1-pentene), and they are summarized in *Table 1*. Despite the discrepancies, all the studies agree that the density of the crystal is comparable to or less than that of the amorphous phase. This unusual property raises the question of whether gas solubility can occur in such a low density crystal.

The notion of small molecules entering the crystalline regions of polymers has been alluded to in the literature. Studies of poly(phenylene oxide) suggest that upon crystallization from solution, solvent molecules may be

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Table 1 Densities of poly(4-methyl-1-pentene) reported by previous studies

	Density (g cm^{-3})		
Reference	Amorphous	Sample	Crystal
Natta *et al.*, 1955[15]		0.831	
Frank *et al.*, 1959[16]		0.847	0.813
Griffith and Ranby, 1960[17]	0.838[a]		0.828
Ranby *et al.*, 1962[18]	0.839[a]	0.828[b]	
Litt, 1963[19]			0.832
Wunderlich, 1973[14]			0.822
Zoller, 1977[20]		0.835[c]	0.827
Kusanagi *et al.*, 1978[21]		0.830	0.828

[a] These samples were quenched and assumed to be fully amorphous
[b] This sample was reported to be 78% crystalline
[c] This sample was quenched but still partially crystalline

incorporated in the crystal lattice[22-24]. Subsequent drying of these materials creates imperfections in the crystal structure which have been attributed to the removal of the solvent molecules from the crystal[24]. Other studies involving the oxidation of polyolefins revealed an unusually large consumption of oxygen in semicrystalline PMP samples[25-27] which led to the conclusion that the crystalline regions of PMP must be permeable to oxygen. However, each of the above examples fails to provide any direct evidence or quantitative assessment for crystal phase solubility or transport. The purpose of this study was to examine directly the possibility of gas transport in the low density PMP crystal through quantitative sorption and permeation measurements using a novel series of samples with widely varying levels of crystallinity.

BACKGROUND

Michaels and coworkers[8,9] measured the solubility of gases in polyethylene as a function of crystallinity and found the Henry's law solubility coefficient, k_D, to be directly proportional to the amorphous volume fraction, α, i.e.

$$k_D = \alpha k_D^* \tag{1}$$

Based on a simple two phase model, k_D^* corresponds to the solubility coefficient for the completely amorphous polymer. Furthermore, since their solubility data (reproduced in *Figure 1* for three representative gases) extrapolate to the origin, they concluded that gases do not dissolve in the crystallites, i.e. $k_D = 0$ at 0% amorphous content.

The simple two phase model can be extended to transport behaviour; however, these properties, unlike the scalar solubility coefficient, have tensorial character and depend on the spatial organization or morphological arrangement of the phases. Since the permeability coefficient, P, is the product of effective solubility and diffusion coefficients, it is possible to write

$$P = \alpha k_D^* D \tag{2}$$

when equation (1) applies, i.e. there is no solubility in one of the phases. For this simple model, the effective diffusion coefficient, D, can be written in terms of the diffusion coefficient in the amorphous phase, D^*,

$$D = \kappa D^* = \frac{D^*}{\tau} \tag{3}$$

and a structural factor, κ, that depends on α and the shape and orientation of the crystals or alternately, a tortuosity factor, τ[7,8,28]. In either case, it is assumed that the amorphous phase has its own properties independent of influence by the crystalline phase and that the latter is impermeable. However, Michaels and coworkers found that although equation (1) adequately describes solubility, the situation is more complex for transport. It appears that the crystalline regions do exert some influence on the transport characteristics of the amorphous region, and a chain immobilization factor, β, was added to equation (3) to account for this[8,10], i.e.

$$D = \frac{D^*}{\tau\beta} \tag{4}$$

The factor, β, accounts for restricted segmental mobility of amorphous chains near the amorphous–crystalline interface due to the crosslinking-type action of the crystallites. Equations 1 and 4 have been used in subsequent studies to analyse sorption and diffusion in other semicrystalline polymers such as polypropylene[29] and poly(ethylene terephthalate)[11,12].

In 1959 Frank, Keller and O'Connor[16] used X-ray diffraction to characterize the crystals of PMP. They described the chains as having a helical conformation with seven repeat units in two turns of the chain. The unit cell is tetragonal with the dimensions, $a = 18.66$ Å and $c = 13.80$ Å, which have been confirmed by other reports[19,21]. Frank *et al.* proposed a uniform arrangement of the side groups in order to accommodate the four chains in the unit cell. However, a study by Litt[19] in 1963 revealed lack of symmetry in the crystal, and he suggested that there could be disorder in the placement of the pendant groups. Further research by Kusanagi *et al.*[21] in 1978 confirmed this observation. They proposed a nonuniform arrangement of the chains in the unit cell as

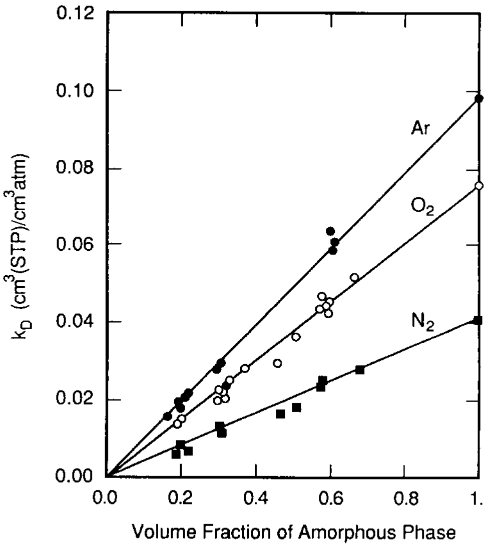


Figure 1 Effect of crystallinity on gas solubility in polyethylene. (Data from Michaels and Bixler[9])

illustrated in *Figure 2*. In addition, they proposed a three-dimensional structural model for the exact placement of each pendant group. *Figure 3* represents the final crystal structure with dashed lines outlining the van der Waals radii of the methylene groups. As illustrated, gaps of almost 4 Å exist between the chain segments in this model, which is consistent with the low crystal density reported for PMP. As a result, Kusanagi *et al.* concluded that the low density is due to the loosely packed crystal structure. The vacant spaces apparent in *Figure 3* suggest the possibility that small gas molecules could be accommodated in the PMP crystal.

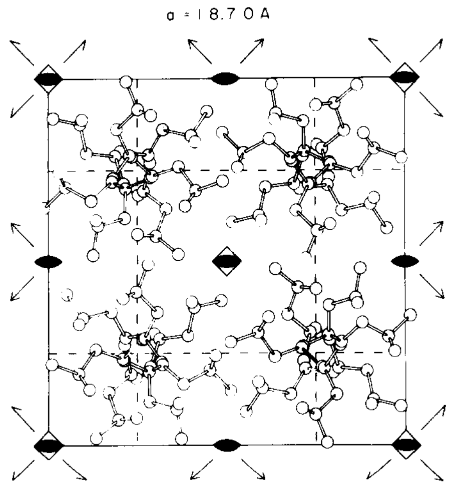


Figure 2 Crystal structure of isotactic poly(4-methyl-1-pentene) showing four chains in the unit cell. Reprinted with permission of the Journal of Polymer Science, copyright 1978, John Wiley and Sons, Inc.

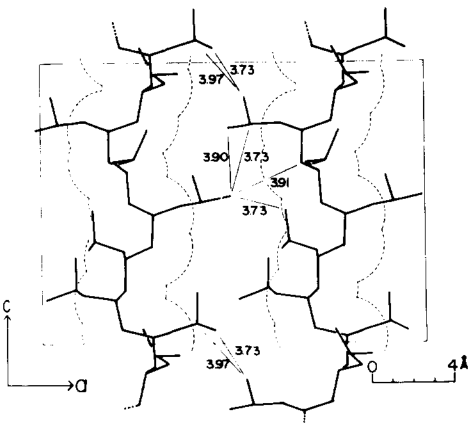
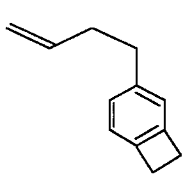


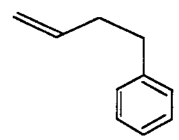
Figure 3 Schematic representation of a side view of two adjacent chains in the poly(4-methyl-1-pentene) crystal. -----, indicate the van der Waals radii (2.0 Å) of the methylene and methine groups in the skeletal chain. Reprinted with permission of the Journal of Polymer Science, copyright 1978, John Wiley and Sons, Inc.

EXPERIMENTAL

Polymers of 4-methyl-1-pentene from two different sources were used in this work. The first was obtained from Polysciences, and based on knowledge of commercial products it is likely that this material may contain a small amount of some comonomer. The second was a series of experimental polymers prepared in the laboratories of the Shell Development Co. using Ziegler–Natta polymerization[30]. Varying amounts of the comonomer, 4-(3-butenyl) benzocyclobutene, or 4BBC, were introduced for thermal crosslinking and hence reduction of crystallinity. 4BBC has the following structure:



As a control, a structurally similar but non-reactive compound, 4-phenyl-1-butene or 4PB, was incorporated into one sample. 4PB has the following structure:



These materials and the films made from them are described in *Table 2*.

The commercial polymer was compression moulded at 250°C for 8 min into film. Various cooling treatments were used to obtain different crystallinities. The film designated **Q** was taken directly from the mould and quenched in ice water. Film **S** was slowly cooled for 7 min using the water cooling cycle of the moulding machine. Film **A** was taken directly from the mould at 250°C and placed immediately in an annealing oven at 126°C for 3 days. It was then allowed to cool to room temperature.

Table 2 Description and characteristics of the materials used to investigate gas sorption and transport in poly(4-methyl-1-pentene)

Designation	Description	ΔH_f (cal gm^{-1})	X-ray cryst. (%)	T_g (°C)	T_m (°C)
Q	Commercial material[a] (quenched)	7.5	53.6	30	233
S	Commercial material[a] (slow cooled)	9.0	61.2	27	233
A	Commercial material[a] (annealed)	11.2	66.4	22	234
H	Homopolymer (experimenta)	10.1	62.7	37	243
1.0X	1.0 wt% (0.53 mol%) 4BBC[b]	7.6	49.7	37	229
2.5X	2.5 wt% (1.3 mol%) 4BBC	5.7	41.8	40	223
10X	10 wt% (5.6 mol%) 4BBC	3.0	21.6	53	209
2.5R	2.5 wt% (1.6 mol%) 4PB[c]	9.1	55.8	34	238

[a] This poly(4-methyl-1-pentene) material was obtained from Polysciences and may contain a small amount of an unspecified comonomer
[b] 4BBC designates the reactive comonomer, 4-(3-butenyl)benzocyclobutene
[c] 4PB designates the unreactive comonomer, 4-phenyl-1-butene

The crystalline fraction of these films ranged from about 50–75%.

The five experimental PMP samples were dissolved in hot chloroform and cast onto glass plates. The films were dried for at least 2 days under ambient conditions to remove the solvent and then were placed in the compression moulder at 280°C for 20 min. They were cooled to ambient conditions using the water cycle of the moulding machine. At 280°C, the 4BBC comonomer units react to form crosslinks between chain segments[30], which in turn reduce the ability of the polymer to crystallize[31,32]. A possible crosslinking reaction scheme reported in the literature is shown in *Figure 4*[33–35], although the exact mechanism and structures are unknown[35]. The films containing the 4BBC had crystallinities ranging from 20–50%. The film designated **2.5R**, containing the unreactive comonomer, had considerably higher crystallinity than the film based on a corresponding amount of reactive comonomer. This material was included in the sorption and transport experiments to determine the specific chemical effect, if any, that a comonomer similar to 4BBC would have on these properties beyond the physical issue of crystallinity.

Thermal analysis of the films was carried out using a Perkin–Elmer DSC-7 at a heating rate of 20°C min^{-1}. The glass transition temperatures (T_g) were computed as the onset temperature of the transition region. The T_g values reported in the literature for various samples of PMP range from 15–34°C[17,18,20,36]. All the T_g values for the films in this study were close to the experimental temperature of 35°C, except for the **10X** film. Since the glass transition is associated with the onset of large scale motions of the polymer chain segments, factors such as crosslinking, that reduce chain mobility, increase the T_g. Melting temperatures were measured as the peak of the melting endotherm, and heats of fusion were calculated from the area under the melting peak. An example of a d.s.c. scan for the PMP homopolymer is shown in *Figure 5* where the transitions are labelled. To illustrate the reduction in crystallinity caused by crosslinking, a thermogram for the **2.5X** polymer powder is illustrated in *Figure 6*. In the first scan, the unreacted powder was heated to the reaction temperature of 280°C and held there for 15 min. This sample was then quenched and reheated. The reduction in the endotherm area caused by crosslinking is readily apparent in the second scan.

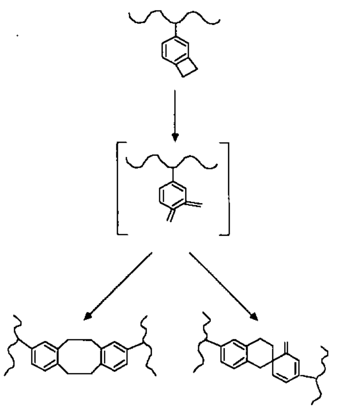


Figure 4 A possible crosslinking reaction scheme of the 4BBC comonomer units undergoing a ring-opening mechanism

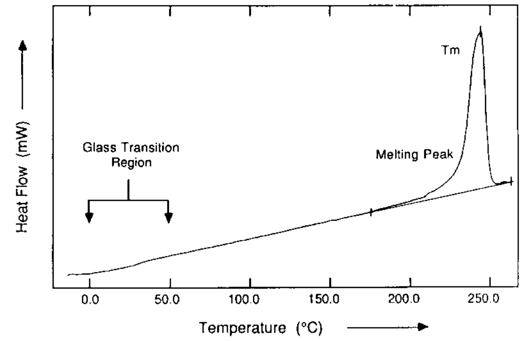


Figure 5 D.s.c. thermogram for the PMP experimental homopolymer

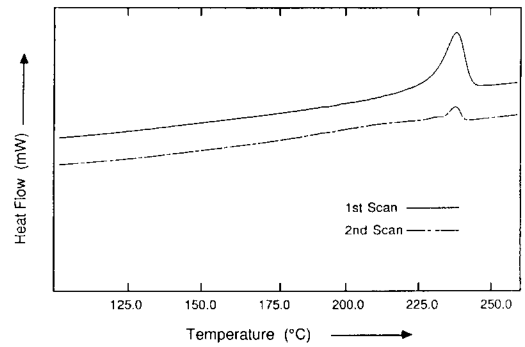


Figure 6 D.s.c. thermogram for the **2.5X** polymer before and after crosslinking (1st and 2nd scans, respectively) showing the reduction in the melting endotherm (hence, reduced crystallinity) caused by crosslinking

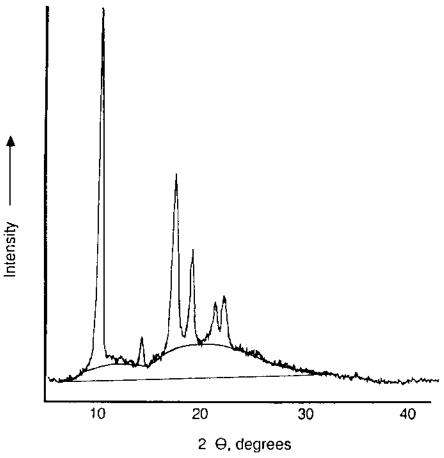


Figure 7 X-ray diffraction scan for the PMP experimental homopolymer

Powder X-ray diffraction scans were made on an IBM Series/1 automated Phillips diffractometer fitted with a diffracted beam monochromator and Cu Kα radiation. A typical result is shown in *Figure 7* where the line dividing the amorphous and crystalline contributions was drawn comparable to others in the literature[36,37].

The apparatus and techniques used in the sorption and transport experiments were similar to those described elsewhere[38] in greater detail. All measurements were made at 35°C.

RESULTS AND DISCUSSION

Crystallinity determination

To learn whether gas molecules can dissolve or diffuse in the crystals of PMP requires accurate and absolute determination of the fraction of each sample that is crystalline or amorphous. Heats of fusion, ΔH_f, can be accurately measured by d.s.c. and values for each film are listed in *Table 2*. However, to convert these into a fractional crystallinity, w_c, via

$$w_C = \frac{\Delta H_f}{\Delta H_f^\circ} \tag{5}$$

requires an accurate value of the heat of fusion for the 100% crystalline polymer, ΔH_f°. A wide range of values for this parameter have been reported in the literature for PMP (see summary in *Table 3*) and Zoller *et al.*[42] have recently published an excellent review dealing with most of them. They deduced a value of 14.8 cal g^{-1}, which is much lower than those reported previously, using what appears to be a very careful investigation based on use of the Clapeyron equation. At about the same time He and Porter[37] used a different methodology and deduced a value which is more comparable to the value of Zoller *et al.* than those reported earlier. Before adopting a value for use in this work, additional experiments were performed to clarify the issue.

X-ray diffraction patterns were obtained for each film specimen in order to provide an independent assessment of crystallinity. The amorphous contribution was drawn as shown in *Figure 7* using previous results as a guide[36,37]. The per cent crystallinity was then computed from area ratios in the usual way[43], and the results are summarized in *Table 2*. In *Figure 8*, the values of ΔH_f determined by d.s.c. for each sample are plotted *versus* the per cent crystallinity determined by X-ray diffraction. The line shown was drawn from the origin to the value of 14.8 cal g^{-1}, given by Zoller *et al.*, at 100% crystallinity. This appears to be a very satisfactory representation of these data, hence the Zoller *et al.* result for ΔH°_f was adopted in this study to compute crystallinity according to equation (5). Using this heat of fusion, the degrees of crystallinity for the uncrosslinked compression moulded films ranged from 50–75% which agrees with levels measured by n.m.r. and density techniques reported for other compression moulded PMP films[44].

Table 3 Heat of fusion values for 100% crystalline poly(4-methyl-1-pentene)

Method of determination	ΔH_f° (cal g^{-1})	Reference
Cohesive energy density	58	Schaefgen[39]
Copolymer melting points	30–34	Isaacson *et al.*[40]
Melting point depression by diluent	29	Karasz *et al.*[36]
Clapeyron equation	28	Jain *et al.*[41]
Clapeyron equation	14.8	Zoller *et al.*[42]
WAXD and DSC	12.5	He and Porter[37]

Gas sorption

Carbon dioxide and methane are considerably more soluble in polymers than N_2, He or H_2. Since the solubility of all gases in PMP is relatively low compared to glassy polymers, CO_2 and CH_4 were selected for these

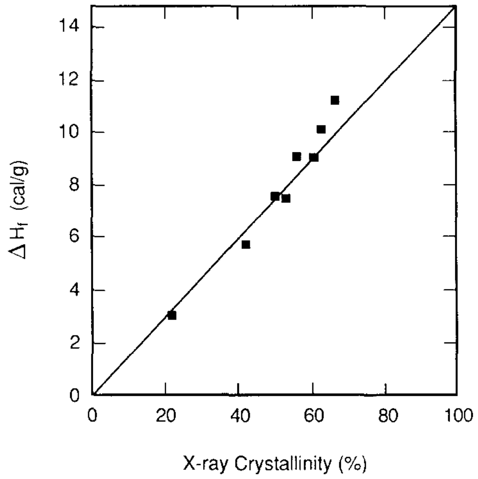


Figure 8 Heats of fusion of PMP materials determined by d.s.c. *versus* per cent crystallinity from X-ray diffraction. Solid line drawn to go through the origin and a heat of fusion of 14.8 cal g^{-1} at 100% crystallinity

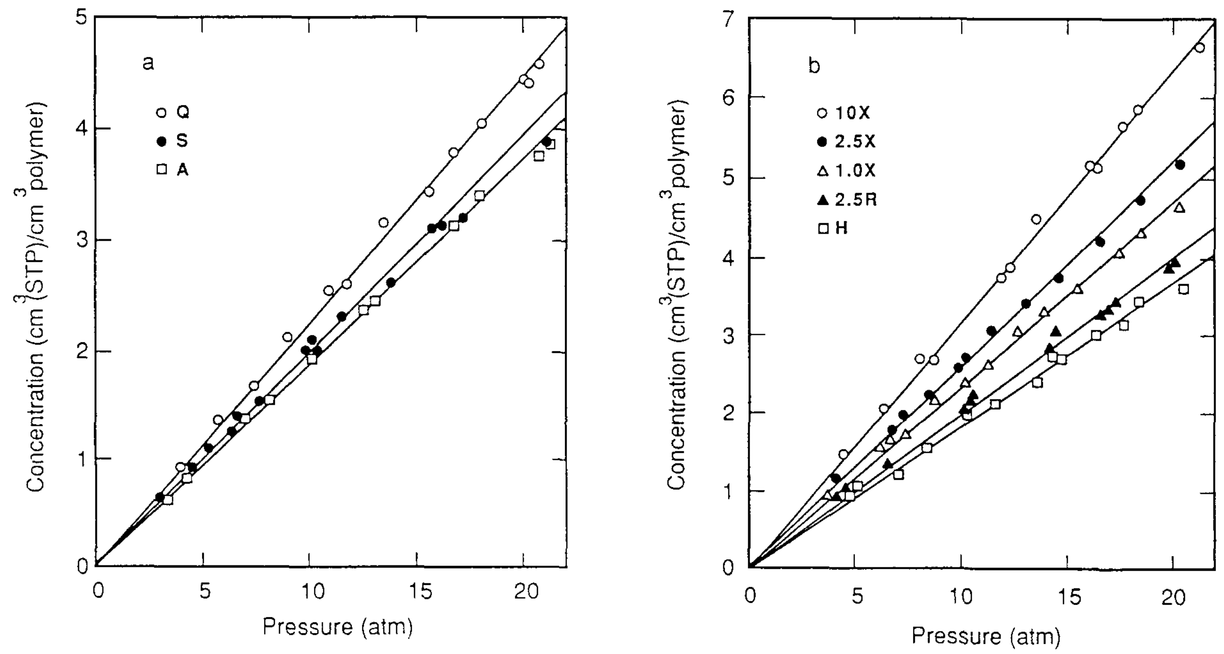


Figure 9 Sorption isotherms measured at 35°C for CH_4 in (a) the commercial PMP films and (b) the experimental polymers

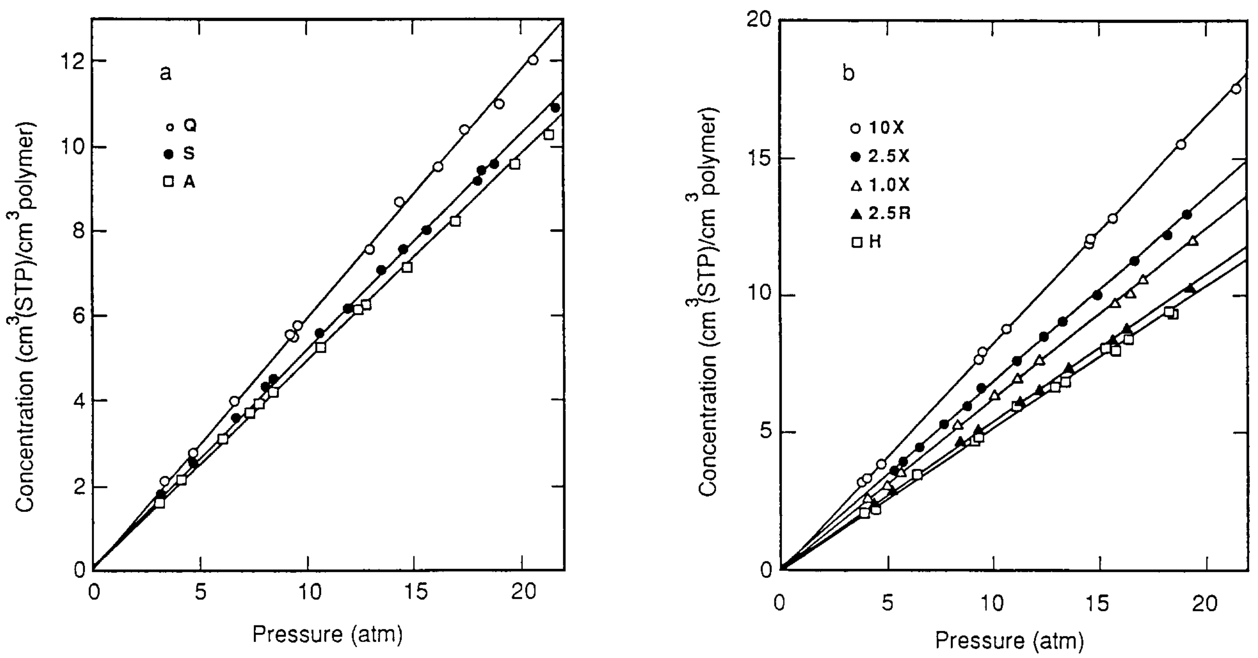


Figure 10 Sorption isotherms measured at 35°C for CO_2 in (a) the commercial PMP films and (b) the experimental polymers

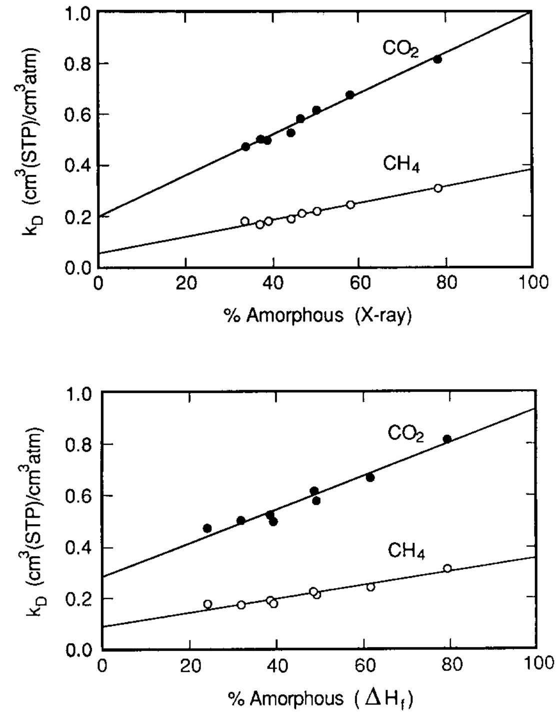


Figure 11 Effect of amorphous content on gas solubility in the PMP materials

Table 4 Gas solubilities at 35°C for the amorphous and crystalline phases of poly(4-methyl-1-pentene) deduced from linear regression analysis

Method of crystallinity determination	Solubility coefficient, k_D (cm³ (STP)/cm³ atm)			
	Amorphous phase		Crystalline phase	
	CO_2	CH_4	CO_2	CH_4
ΔH_f	0.93	0.351	0.28±0.03	0.095±0.013
X-ray	0.99	0.378	0.20±0.02	0.060±0.010

experiments to enhance measurement accuracy. The sorption isotherms obtained (*Figures 9* and *10*) follow a linear relationship, or Henry's law,

$$C = k_D p \qquad (6)$$

as expected for polymers close to or above their T_g[45]. The Henry's law coefficients, k_D, computed from these isotherms are plotted in *Figure 11 versus* the amorphous content of the films measured by both X-ray and calorimetry. The data follow a linear trend as found for polyethylene (*Figure 1*); however, the PMP data clearly extrapolate to a nonzero value for the 0% amorphous phase limit. Based on a two-phase model, this means that CO_2 and CH_4 are soluble in the 100% crystalline material. The intercepts and standard deviations listed in *Table 4* were computed using statistical analysis. These results show that, regardless of the method used to measure crystallinity, the k_D intercept at 0% amorphous content is a significant value, and it is reasonable to conclude that the gas molecules can dissolve in the PMP crystals. However, the solubility coefficients determined in this way for the amorphous region are four to five times larger than for the crystal.

Gas permeation

Permeability coefficients for He, H_2, N_2, O_2, CH_4 and CO_2 were measured at 1 atmosphere and 35°C for each PMP film, and the results are summarized in *Table 5*. These results agree favourably with typical values reported in the literature for N_2 and O_2, e.g. 7 and 32 Barrers respectively[46–48]. However, oxygen permeabilities as high as 65–66 Barrers (10^{-10} cm³ (STP). cm/cm². sec. cmHg) have been reported for a commercial grade of poly(4-methyl-1-pentene) called TPX[49,50]. At this point, it should be mentioned that PMP is an attractive material for membrane-based air separations because it has a high oxygen permeability and a significant O_2/N_2 selectivity.

Table 5 Permeability coefficients for poly(4-methyl-1-pentene) at 1 atm and 35°C

Designation	Crystalline fraction	Permeability, $P \times 10^{10} \left[\frac{\text{cm}^3(\text{STP})\cdot\text{cm}}{\text{sec}\cdot\text{cm}^2\cdot\text{cm Hg}}\right]$ H_2	He	N_2	O_2	CH_4	CO_2
Q	0.51	146.0	111.9	9.26	34.2	19.8	107.5
S	0.61	125.0	95.4	6.74	27.0	14.9	84.6
A	0.76	126.0	88.9	5.93	25.4	13.0	73.8
H	0.68	140.2	107.9	6.68	28.5	14.2	81.7
1.0X	0.51	136.4	103.9	7.04	29.4	15.4	88.4
2.5X	0.38	122.2	91.2	6.55	26.5	14.6	86.0
10X	0.20	97.5	76.6	5.02	20.4	10.5	67.9
2.5R	0.61	130.7	99.7	6.32	27.3	13.8	80.4

Table 6 Ideal separation factors for the poly(4-methyl-1-pentene) films

Designation	Crystalline fraction	Selectivity, P_A/P_B P_{He}/P_{CH_4}	P_{O_2}/P_{N_2}	P_{CO_2}/P_{CH_4}
Q	0.51	5.65	3.69	5.43
S	0.61	6.40	4.01	5.68
A	0.76	6.84	4.28	5.68
H	0.68	7.60	4.27	5.75
1.0X	0.51	6.75	4.18	5.74
2.5X	0.38	6.25	4.05	5.89
10X	0.20	7.30	4.06	6.47
2.5R	0.61	7.22	4.32	5.83

Table 6 lists ideal separation factors defined as the ratio of pure gas permeability coefficients for three gas pairs. For most membrane materials, the selectivity is lower the higher the permeability. This trend is also observed for the PMP films. However, for gas pairs which have similar molecular sizes (i.e. CO_2/CH_4 and O_2/N_2), the selectivity varies much less with crystallinity than for the He/CH_4 pair. Michaels and Parker found similar results for polyethylene[8]. They argued that the selectivity for a given gas pair would not vary with crystallinity if the only effect of crystallites were to reduce the volume of material where solubility is possible and to increase the effective path length for diffusion. The selectivity for He/CH_4 increased significantly with crystallinity, and from this they concluded that the crystallites also restrict amorphous chain mobility, with a more pronounced effect for larger gas molecules. In the case of PMP, permeation in the crystal regions could also account for some of the variation in selectivity with crystallinity, as discussed later.

The gas permeability coefficients measured in this study vary considerably with the crystalline content of the PMP films as shown for carbon dioxide in *Figure 12*. Two trends are apparent. First, P decreases with increasing content of the crosslinking comonomer. Evidently, the crosslinks hinder diffusion by reducing chain mobility in the amorphous phase. Second, for the uncrosslinked samples (right-hand half of *Figure 12*), P decreases as the level of crystallinity increases. This observation appears to parallel the results and conclusions given by Michaels and coworkers[8-10] for semicrystalline polyethylene. However, a simple extrapolation of the data in *Figure 12* would most likely result in a finite permeability coefficient at 100% crystallinity for PMP.

Transport model analysis

In order to explore more carefully the possibility of transport in PMP crystals, transport models for two phase materials were used to analyse the data. Petropoulos[51] has conducted a comprehensive review and commentary on the various equations for describing permeation in binary composite materials. In these transport models the two phases are assumed to be distinct, noninteracting regions whose individual properties are well-defined and independent of the properties or arrangement of these phases in the composite. This is an idealistic view of semicrystalline polymers since it is well known that crystallites can have a significant effect on transport in the amorphous phase as explained previously. However, in order to obtain a basic understanding of the effect of the crystallites on the transport process, these models are adequate.

Two of the equations proposed by Petropoulos were chosen for analysis of the PMP permeation data. The first was originally developed by Maxwell[28] for a dilute dispersion of spheres of component **A** in a continuum of **B**

$$\frac{P}{P_B} = 1 + 3v_A\left[\frac{(\gamma+2)}{(\gamma-1)} - v_A\right]^{-1} \qquad (7)$$

where P is the overall permeability for the material, P_B is the permeability in the continuous phase, v_A is the volume fraction of the dispersed phase and γ is equal to P_A/P_B, or the ratio of permeability coefficients for the two phases. For the semicrystalline PMP films we may assume that the dispersed particles are the crystallites and the continuous region is the amorphous phase. One of the restrictions governing the use of the Maxwell equation is that the particles must be sufficiently separated so each one does not interfere with the flow patterns of its neighbours. However, Petropoulos points out that this equation may apply at higher particle concentrations, regardless of the particle shape, as long as the particles are isometric and uniformly packed. Petropoulos also outlined several other formulas which can describe more concentrated dispersions. For example, the following equation was developed by Higuchi[52,53] for a random

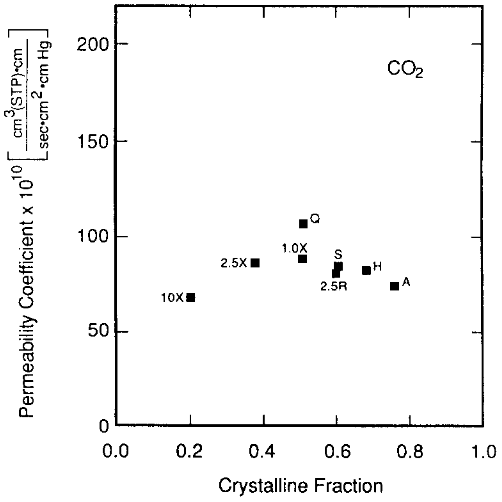


Figure 12 Effect of crystallinity and crosslinking on gas permeation in PMP

dispersion of spherical particles,

$$\frac{P}{P_B}=1+3v_A\left[\frac{(\gamma+2)}{(\gamma-1)}-v_A-K(1-v_A)\frac{(\gamma-1)}{(\gamma+2)}\right]^{-1} \quad (8)$$

The empirical constant, K, was found by Higuchi to have a value of 0.78.

Nonlinear regression was used to fit the limited PMP data to the Maxwell and Higuchi equations in order to obtain the parameters P_B and γ[54]. Since crosslinking *per se* seems to have a more influential effect on P than simply the reduction in crystallinity it causes, only the data for the uncrosslinked films were considered in this analysis. In addition, the annealed sample, **A**, had a higher permeability than would be predicted for an unannealed sample with the same level of crystallinity. This observation is consistent with others reported in the literature[13,29]. For this reason, sample **A** was also not included in the regression analysis. However, permeability coefficients measured for a second slow cooled film, designated **SQ**, were included.

The curves in *Figure 13* are the results of nonlinear regression used to fit the two transport equations to the carbon dioxide data. There is no significant difference between the curves obtained using the two models. The data point for the annealed sample, although not used in the analysis, is included in the figure for comparison. The parameters, P_A, P_B and γ, were deduced for each gas, and the results from the Maxwell equation are listed in *Table* 7. The results of this analysis suggest that the permeability coefficients in the crystalline phase of PMP are non-zero although smaller than those for the amorphous phase. In addition, the transport in the crystalline phase appears to offer some selectivity advantage. For example, the ratio of O_2 to N_2 permeability in the crystal is approximately 8 compared to about 2.9 in the amorphous phase. However, the statistical analysis indicated a significant uncertainty in the parameter estimation, so these numbers must be interpreted with caution.

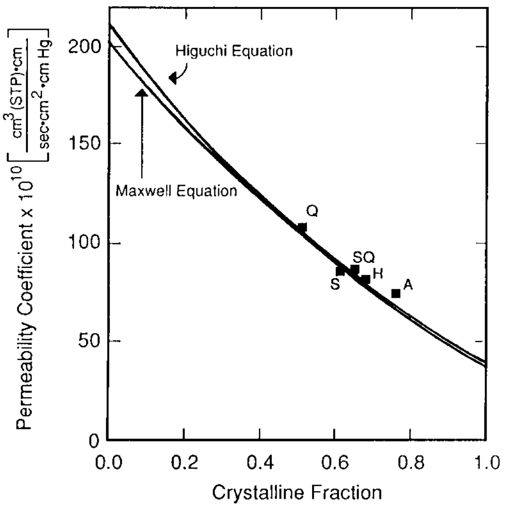


Figure 13 Results of nonlinear regression analysis of the permeation data for the uncrosslinked PMP samples

Table 7 Permeability coefficients computed from the Maxwell equation for the amorphous and crystalline phases of poly(4-methyl-1-pentene)

	Permeability, $P\times10^{10}\left[\frac{\text{cm}^3(\text{STP})\cdot\text{cm}}{\text{sec}\cdot\text{cm}^2\cdot\text{cm Hg}}\right]$		
Gas	Amorphous phase	Crystalline phase	$\gamma = P_{\text{Cryst.}}/P_{\text{Amorph.}}$
He	130	88	0.68
H_2	170	116	0.68
N_2	19	2	0.10
O_2	55	17	0.31
CH_4	42	4	0.10
CO_2	200	38	0.19

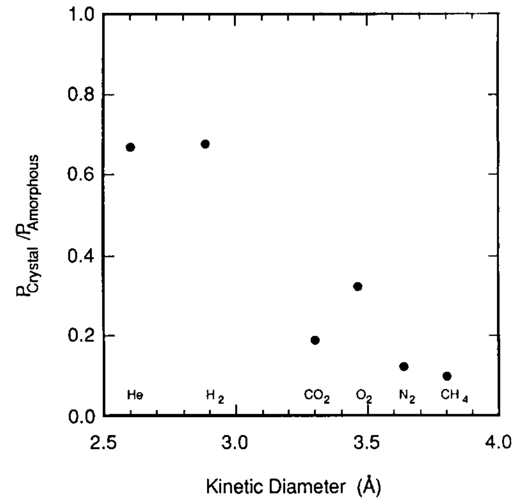


Figure 14 Effect of molecular size on the permeation of gases in the crystal relative to permeation in the amorphous phase

The uncertainty of these model parameters stems from two major sources. First, there is a limited amount of data that covers only a small range of the composition spectrum. In order to make the extrapolation more accurate, data would be needed for samples with lower crystallinities which are free of the complications caused by crosslinking. The second factor is the assumption on which the two equations are based, e.g. the two phases do not interact. In the case of semicrystalline polymers, the crystallites are believed to act as physical crosslinks[10]. Some of the reduction in permeability with increasing crystallinity may be due to this effect, and as a result, transport in the crystal would be even higher than predicted by the regression analysis.

The results in *Table* 7 suggest that the molecular size of the gas has a significant effect on its transport rate in the crystal. *Figure 14* shows the parameter, γ, i.e. the ratio of the crystalline to the amorphous permeability coefficients, decreases as the kinetic diameter of the diffusing molecule increases. The ratio approaches zero near 3.8–4.0 Å, which is similar to the maximum gap sizes between polymer chains in the PMP crystal as seen in *Figure 3*. Because of the low amplitude of the thermal motions in the crystal relative to those in the amorphous phase, it is reasonable that this ratio should become essentially nil when the penetrant molecule is larger than the free space available in the crystal.

The diffusion coefficients given in *Table 8* were calculated for CO_2 and CH_4 in the amorphous and crystalline phases of PMP using the relation

$$P=k_D D \quad (9)$$

These are approximate values, since both P (*Table 7*) and

Table 8 Approximate diffusion coefficients for the amorphous and crystalline phases of poly(4-methyl-1-pentene)

Gas	Diffusion coefficient, $D \times 10^8$ cm^2 s^{-1}	
	Amorphous	Crystalline
CO_2	164	103
CH_4	91	32

k_D (*Table 4*) for pure phases were obtained by extrapolation. The calculations most likely provide a quite reasonable estimate for the amorphous region, but those for the crystal are undoubtedly not as accurate.

Diffusion of gases in the PMP crystallites, might be compared with that in inorganic crystalline structures such as zeolite molecular sieves. An excellent review of diffusion in zeolites has been given by Ruthven[55]. Using uptake rate experiments, Yucel and Ruthven[56–58] investigated gas diffusion in **4A** and **5A** zeolites, having effective apertures of about 3.8 Å and 4.2 Å, respectively, which are close to the gap sizes in the PMP crystal. From their data, one can estimate concentration corrected diffusion coefficients for CO_2 at 35°C of 1.2×10^{-9} cm^2 s^{-1} for the **4A** and 1.3×10^{-8} cm^2 s^{-1} for the **5A** zeolites[58]. Similarly, a corrected diffusion coefficient for CH_4 in the **4A** zeolite is approximately 7×10^{-11} cm^2 s^{-1} (ref. 56). However, diffusion coefficients from n.m.r. experiments for CH_4 in the **4A** zeolite system are near 10^{-7} cm^{2}s^{-1} at 140 K and have a low activation energy[59].

CONCLUSIONS

The results of this study clearly indicate that gases such as CO_2 and CH_4 can dissolve in the crystals of poly(4-methyl-1-pentene) at about 1/3 to 1/4 the level they do in the amorphous phase. This can be attributed to the very open structure of the PMP crystal where there are gaps between the chains of sufficient size to accommodate small gas molecules. This is in strong contrast to other polymers such as polyethylene where the crystal is on the order of 15% more dense than the amorphous phase, thus presenting a relatively impenetrable phase to gas molecules. Extrapolation of limited transport data also suggests that diffusion occurs at finite rates in PMP crystals, although the results obtained in this way must be regarded as very approximate. Nevertheless, the estimates found show that the ratio of permeability coefficients for the two phases depends on molecular size of the gas and appears to go to zero at the point where the molecules are comparable in size to the gaps in the crystal.

This study was possible because of the capability to vary crystallinity over a wide range. In previous studies on polyethylene[8–10], this was achieved through short chain branching. In this work, thermal treatment and crosslinking were used. The crosslink units do not seem to affect sorption in any way except by reducing crystallinity; however, they have a profound effect on permeation. This is due to physical restrictions on the mobility of chain segments as opposed to any chemical effects caused by the introduction of the comonomer, since no significant differences in transport behaviour were observed between the PMP homopolymer and films containing 2.5 wt% of a similar but unreactive comonomer.

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