Effect of casting solvent on the permeability of poly(4-methyl-1-pentene)

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The permeability of gases in poly(4-methyl-1-pentene) (PMP) films cast from solution depends strongly on the casting solvent used. Permeability coefficients for several gases were measured for PMP films cast from six solvents and for a film prepared from the melt. Sorption isotherms were measured for selected gas–film pairs. Films cast from decalin, xylene and chloroform have lower permeation rates relative to the melt-prepared film. Films cast from cyclopentane, cyclohexane and carbon tetrachloride have permeability coefficients similar to that for the melt-processed film. The differences may be as great as six-fold. X-ray diffraction and thermal analysis were used to characterize the films. It is shown that the casting solvent influences which crystalline modification is formed and the spatial arrangement of the crystallites within the film. The films with very low gas permeability coefficients have a strong preferential orientation of the crystallites with the chain axis normal to the film surface. It is suggested that in these cases, some single crystals were formed during casting which aligned preferentially in the film to give a long tortuous path for permeation of gas molecules. The relative rate of gas transport in the unusually open crystals of PMP is discussed.

(Keywords: gas transport; crystallites; X-ray diffraction; poly(4-methyl-1-pentene))

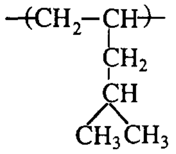
INTRODUCTION

Recently, poly(4-methyl-1-pentene) (PMP) has been used in this laboratory as the permselective layer in composite membranes[1,2]. PMP is soluble in a number of solvents, which can be used to form films of this polymer. During the course of selecting the appropriate solvent for composite membrane fabrication, some distinct differences in films formed from various solvents were noticed. PMP films cast from certain solvents are opaque, whereas other solvents form transparent films. Gas permeation measurements indicated very substantial differences in the transport properties of these films. The purpose here is to report these observations and to offer a possible explanation for the differences found. Permeability measurements were made for PMP films cast from six solvents and for a film prepared from the melt, which served as a basis for comparison. X-ray diffraction and thermal analysis were used to characterize the solvent-cast films.

BACKGROUND

PMP is a semicrystalline polymer. Sorption and transport processes in such polymers are generally treated in terms of a simple two-phase model: namely, a crystalline phase dispersed in an amorphous matrix. It is generally thought that penetrant molecules are insoluble in polymer crystallites and are unable to diffuse through the crystalline phase[3–6]. Thus, when gases permeate through semicrystalline polymers, the penetrating molecules are confined to the amorphous regions between crystallites. The crystallites decrease the permeability by reducing the volume of polymer available for penetrant solution and, as illustrated in *Figure 1*, by constraining diffusion to take place along irregular tortuous paths between the crystallites. The reduction in solubility is directly proportional to the volume fraction of crystalline phase[7]. The reduction in diffusivity, on the other hand, is a function of the shape and spatial arrangement of the crystallites, as well as their volume concentration[3–6,8–12].

PMP is unusual in that the crystalline region has been reported to be less dense than the amorphous phase[13,14]. The bulky pendant group in the repeat unit of PMP, shown below:



$$-\!\!\left(CH_2-\underset{\substack{|\\CH_2\\|\\CH\\\diagup\ \diagdown\\CH_3\ \ CH_3}}{CH}\right)\!\!-$$

inhibits close packing of the polymer chains and results in a low-density crystal with gaps of almost 4 Å between the chain segments[14–16]. Such gaps are large enough to accommodate small gas molecules, and Puleo and Paul[17] recently showed evidence that carbon dioxide and methane can dissolve and diffuse in the crystal. As the size of the penetrant molecule approaches the chain segment gap size, diffusion in the crystal is no longer possible. This is in sharp contrast with the accepted notion that crystallites are impermeable to diffusing molecules. Of course, in most cases, the crystal may be 10–15% more dense than the amorphous phase.

PMP prepared by melt processing usually gives a crystalline modification designated mod. I that is often

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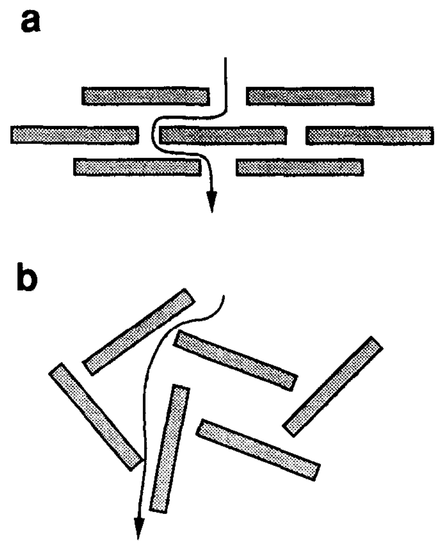

Figure 1 Diffusion in a two-phase system where the particles are considered to be impermeable and can have (a) an ordered or (b) a random spatial arrangement

Table 1 The five crystalline modifications of PMP and their unit-cell structure and dimensions

Mod.	Crystal form	Lattice constants (Å)[a]	
		$a=b$	c
I	Tetragonal	18.66	13.65
II	Tetragonal	19.16	7.12
III	Tetragonal	19.38	6.98
IV	Hexagonal	22.17	6.69
V	Tetragonal[b]	–	–

[a] Data for mods. I–IV from ref. 18
[b] From ref. 19

referred to as the 'usual, or stable, modification'. A total of five crystalline modifications have been reported for PMP. The other four, mods. II–V, are formed from dilute solutions of the polymer in various solvents. The unit-cell structure and dimensions for each crystalline modification are shown in *Table 1*[18–20]. Mod. II was first prepared from xylene solution[20–22], which led to studies on single-crystal formation from other solvents[23]. It is apparent that from a given solvent several modifications or a mixture of modifications can be obtained depending on the dissolution temperature, cooling conditions and polymer concentration[18,23–27]. These parameters apparently affect the conformation of the polymer chains in solution and in turn determine the crystalline modification formed on crystallization. In good solvents, such as decalin and cyclopentane, the PMP polymer chains assume an open random coil conformation. The crystal recovered is loosely folded and irregular. In poorer solvents, such as cyclohexane and xylene, the dissolved polymer is said to have an ordered helical conformation that leads to a regular and more well defined crystal[23,24,28].

EXPERIMENTAL

Materials and solvents

The PMP was purchased from Scientific Polymer Products (Ontario, NY) and was used to prepare films from the six solvents. Catalogue specifications indicate a melt index of 8 and a density of 0.835 g cm^{-3}. As a basis for comparison with the solvent-cast films, the data reported by Puleo[17] on a compression-moulded film are used. This film was prepared from PMP purchased from Polysciences (Warrington, PA) and was compression moulded at 250°C for 8 min and then cooled for 7 min using the water cooling cycle of the moulding machine.

The six solvents, listed in *Table 2*, were of reagent grade or better and were used without further purification.

Equipment

Pure gas permeability coefficients were measured for seven gases using the standard permeation techniques employed in this laboratory[29,30]. Data were collected at 35°C and 2 atm upstream driving pressure.

Methane and carbon dioxide gas sorption measurements were made from 1 to 20 atm at 35°C using a pressure decay sorption cell described elsewhere[30,31].

X-ray diffraction patterns were taken on an IBM Series/1 automated Philips diffractometer fitted with a diffracted beam monochromator and Cu K_α radiation. Scans were made for the polymer films at 40 kV, 40 mA and 2 deg min^{-1}.

X-ray diffraction photographs were taken with a flat-plate camera using nickel-filtered Cu K_α radiation from a Philips X-ray generator at 20 mA and 35 kV. The distance from specimen to film was 4 cm and the exposure time was 2 h. Photographs were taken with the X-ray beam normal (through view: TV) and 90° off-normal (edge view: EV) to the film surface.

Differential scanning calorimetry (d.s.c.) and thermal gravimetric analysis (t.g.a.) were done using a Perkin–Elmer 7-Series Thermal Analysis System. A heating rate of 20°C min^{-1} was used for both d.s.c. and t.g.a.

Film preparation

Solutions of 0.5–2 wt% polymer were prepared by dissolving the PMP pellet at temperatures high enough to give dissolution within 8 h. The warm solution was then cast onto a glass plate at room temperature. The casting procedure was done inside a glove-bag to control the rate of solvent removal. The films were dried for several days at room temperature. Thermal gravimetric analysis confirmed that all the films were free of residual solvent except the one cast from decalin. Decalin has the highest boiling point of all the solvents used (193°C) and t.g.a. showed 3 wt% solvent remaining in the film after drying for several weeks. All films were 1–3 mil (~25–75 μm) in thickness.

RESULTS AND DISCUSSION

Gas sorption and transport

Permeability coefficients of nitrogen, oxygen, helium, hydrogen, methane and carbon dioxide were measured

Table 2 The solvents used to prepare PMP films

Solvent	Formula	Boiling point (°C)
Chloroform	$CHCl_3$	61
Carbon tetrachloride	CCl_4	77
Cyclopentane	C_5H_{10}	81
Cyclohexane	C_6H_{12}	50
p-Xylene	$C_6H_4(CH_3)_2$	138
cis-Decalin	$C_{10}H_{18}$	193

Table 3 Permeability coefficients and ideal selectivities for PMP films cast from various solvents and prepared from the melt

Casting solvent	Crystallinity (%)	Permeability[a]							Selectivity		
		N_2	O_2	CH_4	H_2	He	CO_2	C_3H_8	O_2/N_2	H_2/CH_4	CO_2/CH_4
Chloroform	57	1.1	5.2	2.1	33.2	33.1	15.0	1.9	4.7	15.8	7.2
p-Xylene	62	2.7	12.4	5.2	68.1	59.7	42.6	–	4.6	13.1	8.2
cis-Decalin	65	1.6	7.4	3.6	52.8	49.5	27.8	–	4.5	14.7	7.7
Cyclopentane	41	7.4	27.8	16.9	109.8	84.4	93.8	20.4	3.8	6.5	5.6
Cyclohexane	51	6.5	27.3	13.1	114.0	97.8	83.0	–	4.2	8.7	6.4
Carbon tetrachloride	56	6.0	24.8	13.0	113.1	89.7	77.7	–	4.1	8.7	6.0
Melt processed[b]	61	6.7	27.0	14.9	125.0	95.4	84.6	15.9	4.0	8.4	5.7

[a] Units: 10^{-10} cm^3 (STP) cm/(s cm^2 cmHg) at 35°C and 2 atm
[b] Taken from ref. 17

for the PMP films prepared from the six solvents. Propane permeability coefficients were measured on three of the films. The results are summarized in *Table 3* along with the permeability coefficients for a melt-processed film[17]. The data fall into two distinct groups. The films cast from decalin, xylene and chloroform have significantly lower permeation rates to all gases relative to the film prepared from the melt. The chloroform-cast film has the lowest permeability, while the permeability of the xylene-cast film is slightly higher. Residual solvent in cast films can either depress (antiplasticize)[32] or enhance (plasticize)[33] the gas permeability, so the permeability values shown for the decalin-cast film must be interpreted with caution. Films cast from cyclopentane, cyclohexane and carbon tetrachloride have permeability coefficients similar to that for the melt-processed film. The permeabilities of films cast from cyclohexane and carbon tetrachloride are closest in value to the melt-prepared film. The cyclopentane-cast film has a slightly higher permeability to four of the gases relative to the melt-processed film. Ideal gas selectivity values, listed in *Table 3*, also fall into the same two general groups. The three lower-permeability films have higher selectivities than the films in the other group.

It is worth noting that the low-permeability films cast from chloroform, xylene and decalin were opaque, whereas films cast from cyclopentane and cyclohexane or formed by melt processing were transparent. The carbon tetrachloride film did not follow this correlation as it was opaque yet has a permeability similar to that of the transparent films.

The permeabilities of the films cast from chloroform and cyclopentane are the most extreme. Permeation through chloroform-cast PMP is much slower than for the standard melt-processed films, whereas permeation of several gases through cyclopentane-cast films is slightly faster than for the melt-processed film. Propane (C_3H_8) permeability coefficients were measured for these three films and are shown in *Table 3*. The kinetic diameter of propane, 4.3 Å[34], is the largest of the gases tested and 0.5 Å larger than methane. For cyclopentane-cast and melt-processed PMP films, propane permeation is faster than methane. However, in the chloroform-cast film, the propane permeability is lower than the methane permeability.

Chloroform- and cyclopentane-cast films were annealed at several temperatures between 25 and 160°C for 24 h, after which the oxygen permeability was measured. A new film was used for each annealing temperature. The results are shown in *Figure 2*. The broken line at 27 Barrers indicates the oxygen permeability of the melt-processed PMP. The oxygen permeability of chloroform-cast PMP before any annealing is 5.2 Barrers. The permeability increases as the annealing temperature becomes higher and eventually reaches the permeability of the melt-processed film. Cyclopentane-cast PMP has an oxygen permeability of ~28 Barrers before annealing, and essentially there is no change after annealing at temperatures up to 140°C.

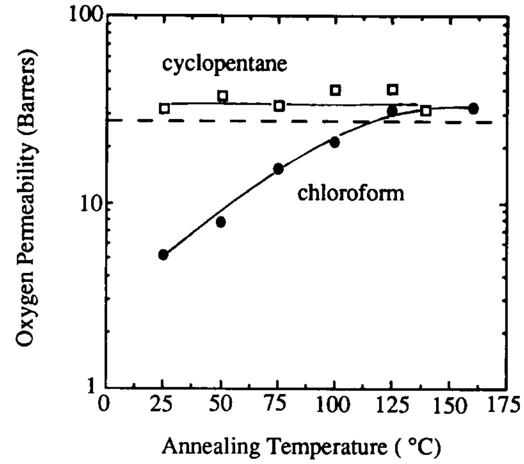

Figure 2 Oxygen permeability at 35°C as a function of annealing temperature for chloroform- and cyclopentane-cast PMP. The broken line indicates the oxygen permeability of melt-processed PMP. A new film was used for each annealing temperature

The dramatic increase in permeability of the chloroform-cast film caused by annealing may be due to partial melting and recrystallization and/or to a reorganization of the crystalline phase. Thermally induced crystal–crystal transformations have been reported where crystalline modifications II, III and IV transform to mod. I at specific temperatures[20–22,24,25,27].

Gas sorption

Methane and carbon dioxide sorption measurements were made at 35°C for the chloroform- and cyclopentane-cast films. The sorption isotherms are shown in *Figure 3* along with those for melt-processed PMP[17]. The isotherms follow a linear relationship between the

Table 4 Transport coefficients, solubility coefficients and ideal selectivities for CO_2 and CH_4 at 35°C in compression-moulded and solvent-cast PMP

Film	P_{CO_2} (Barrers)	$\frac{P_{CO_2}}{P_{CH_4}}$	S_{CO_2} (cm^3/cm^3 atm)	$\frac{S_{CO_2}}{S_{CH_4}}$	D_{CO_2} (10^{-7} cm^2 s^{-1})	$\frac{D_{CO_2}}{D_{CH_4}}$
Melt-processed[a]	85	5.7	0.51	2.6	12.5	2.2
Chloroform-cast	15	7.2	0.40	2.5	2.8	2.9
Cyclopentane-cast	94	5.6	0.58	2.9	12.3	1.8

[a] Data taken from ref. 17

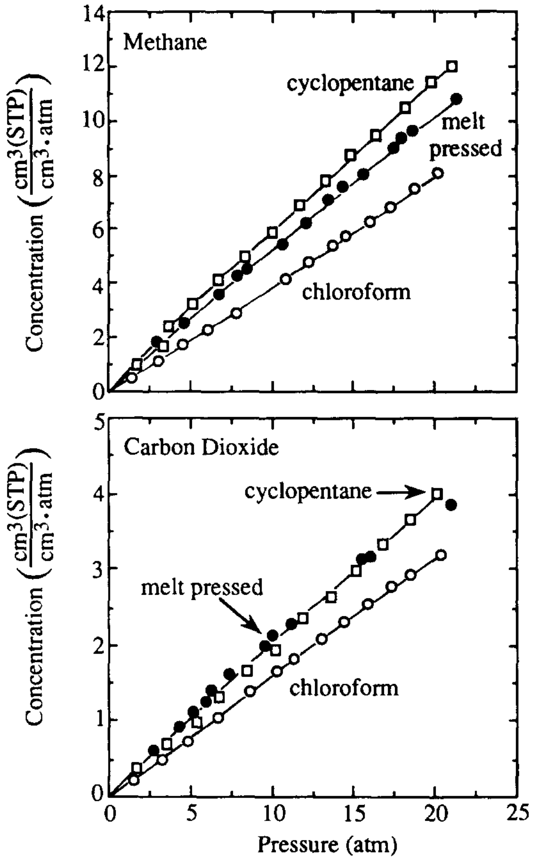

Figure 3 Methane and carbon dioxide sorption isotherms at 35°C for melt-processed PMP and for PMP cast from cyclopentane and chloroform

concentration of gas sorbed, C, and pressure, p:

$$C = Sp \tag{1}$$

expected for polymers near or above their glass transition[35]. The Henry's law coefficients, S, were computed from the isotherms, and the coefficient for carbon dioxide and the ideal solubility selectivity for carbon dioxide to methane are shown in *Table 4*. The diffusion coefficients, D, were determined from the relation between the permeability coefficient, P, and the Henry's law solubility coefficient, S:

$$P = SD \tag{2}$$

The carbon dioxide diffusivity coefficients and the diffusivity selectivity for carbon dioxide to methane are also shown in *Table 4*. These results show that the low permeability of the chloroform-cast film is due mainly to mobility considerations since the diffusion coefficients for the chloroform-cast film are approximately four times lower than those for the other two films. The solubility of methane is slightly higher in cyclopentane-cast PMP than in the melt-processed film while the solubility of carbon dioxide is about the same in each.

The solubility results in *Figure 3* and those presented previously for melt-pressed films[17] cannot be explained fully on the basis of the level of crystallinity of the PMP samples. Methane is about 1.4 times more soluble in the film cast from cyclopentane than in the film cast from chloroform. The amorphous content of the former is 1.37 times greater than that of the latter. However, the ratio of the solubility of the smaller carbon dioxide molecules in these two films is 1.24. The amorphous contents of the chloroform- and the cyclopentane-cast films are larger than those of the melt-pressed film, mentioned in *Table 3*, by factors of 1.1 and 1.5, respectively, yet the solubilities of carbon dioxide and methane are significantly greater in the melt-pressed material. The earlier work of Puleo and Paul[17] suggested that sorption also occurred in the crystal phase of the melt-pressed film. It appears that sorption is considerably less or non-existent in the crystal phase of these solution-cast films, which may reflect higher densities of these crystals.

FILM CHARACTERIZATION

Differential scanning calorimetry

The first heat d.s.c. traces for the six solvent-cast films and for the melt-processed film are shown in *Figures 4* and *5*. The melt-prepared PMP has a single melting peak at 232±2°C, as do films cast from cyclohexane, cyclopentane and carbon tetrachloride (*Figure 4*). The d.s.c. traces for films cast from xylene, decalin and chloroform (*Figure 5*) have more than one melting peak. The xylene-cast film shows a small endotherm at 73°C, while the decalin-cast film has a peak at 115°C. The chloroform-cast film has several smaller peaks from 75 to 140°C. The presence of a second melting endotherm for solvent-cast PMP has been observed by others and was attributed to the transition from one crystalline modification to the usual modification (mod. I) on heating[24,25,27]. The degree of crystallinity was calculated from the endotherm area, or heat of fusion (ΔH_f), of each trace and the heat of fusion for the 100% crystalline polymer of 14.8 cal g^{-1} (refs 17, 36). These values are listed in *Table 3* for comparison with the permeability coefficients. Cyclopentane-cast PMP has the lowest level of crystallinity at 41% and the highest permeability. However, the crystallinity levels of chloroform- and xylene-cast films are similar to that of the melt-processed film, but the melt-pressed film is much more permeable than chloroform- and xylene-cast films. It is clear that a simple difference in the degree of crystallinity is not the only reason for the permeability differences. Evidently,

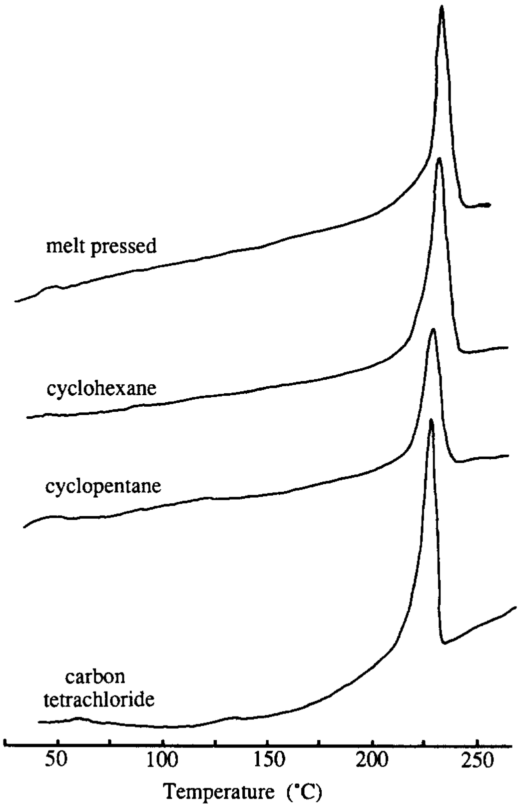

Figure 4 D.s.c. thermograms for melt-processed PMP and for PMP cast from cyclohexane, cyclopentane and caibon tetrachloride

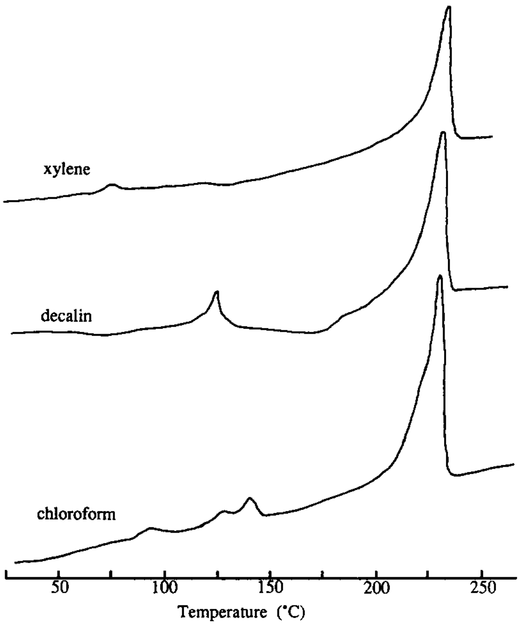

Figure 5 D.s.c. thermograms for PMP cast from xylene, decalin and chloroform

the spatial orientation and shape of the crystallites also play a role.

X-ray diffraction

Figures 6 and *7* show X-ray diffraction patterns for the melt-processed film and the solvent-cast films. The films cast from decalin and xylene had identical patterns and are, therefore, shown as a single curve. The pattern for the melt-prepared PMP matches that previously reported[25]. The solvent-cast films all have their most intense peak at 16.2°±0.2°. Other than this single common feature, the patterns fall into the same two categories observed for the permeability coefficients. The chloroform-, xylene- and decalin-cast films have their second and third most intense peaks at 26.2° and at 13.2°, respectively. In the other group, the cyclopentane- and cyclohexane-cast films have their second and third most intense peaks at 18.5° and at 9.2°, respectively. The pattern for carbon tetrachloride-cast PMP most closely resembles that of the cyclohexane- and cyclopentane-cast films; however, the peak intensities are slightly different.

X-ray patterns for the five PMP crystalline modifications have been reported[18,25]. The X-ray scans reported were taken for PMP crystals recovered from solutions where the polymer concentration was in the same range as that used here for film formation. By comparing the X-ray scans shown in *Figures 6* and *7* with those in the literature, it is possible to classify each film tentatively according to which crystalline modification it has. The lower-permeability films, i.e. cast from chloroform, xylene and decalin, are probably mod. II, mod. III or a mixture of these. The X-ray patterns of the higher-permeability films, i.e. cast from cyclohexane, cyclopentane and carbon tetrachloride, correspond most closely to those for mod. IV and mod. V.

X-ray photographs of the chloroform- and cyclopentane-cast films were taken with the X-ray beam normal (through view: TV) and 90° off-normal (edge view: EV) to the film surface. *Figure 8* shows the photographs for the cyclopentane-cast film. The diffraction haloes observed in both the TV and EV photographs are continuous and of nearly constant intensity around their circumference, which indicates that the crystalline regions are for the most part randomly oriented. The reflections in the EV photograph are slightly more intense than in the TV photograph and there is some arcing, which indicates a slight preferential orientation of the crystallites. The X-ray photographs taken in the TV and EV directions for the chloroform-cast film are shown in *Figure 9*. The reflections in the TV direction again appear as uniform haloes: however, in the EV photograph the reflections are of non-uniform intensity and are discontinuous around the azimuthal angle. These arcs are conclusive evidence for preferred orientation of the crystals present. Comparison of the EV photograph in *Figure 9* with those from the literature for oriented fibres[25] shows that the crystallites are preferentially oriented with the chain axes perpendicular to the film surface.

CONCLUSIONS

The results described here show that the permeability of PMP can vary significantly depending on the casting solvent. PMP films cast from chloroform have an oxygen permeability of 5.2 Barrers, whereas those cast from cyclopentane have an oxygen permeability of 28 Barrers. The casting solvent influences which of the five crystalline modifications is formed and the spatial arrangement of the crystallites within the film. X-ray diffraction photographs showed that there is a strongly preferred orientation of the crystallites in the chloroform-cast film (an example of a low-permeability film) but films cast from cyclopentane (an example of a high-permeability film) are more nearly isotropic, with only a slight tendency for crystallite orientation.

No doubt numerous factors affect the gas permeability of semicrystalline polymers like PMP; however, the following simple hypothesis seems to explain the most extreme results described here. The PMP solutions used to cast films were initially at temperatures and concentrations similar to those used in the literature to form PMP single crystals. For the latter, the solution is held at a temperature a few degrees below the equilibrium polymer melting point of the solution, normally without allowing any solvent evaporation. In film casting, the usual situation is gradual evaporation of solvent to make a more and more concentrated solution that eventually becomes a solid. For typical amorphous, glassy polymers the latter occurs without any phase transition, but this must be a part of the process for film formation from a semicrystalline polymer. In the initial stages of film formation from certain solvents, like chloroform, single crystals of PMP may be formed that aggregate into a mat such that the lateral dimensions of the crystals align within the plane of the final macroscopic film. This would create a structure much like that portrayed in *Figure 1a*, which has a low gas permeability due to the tortuous diffusion path[3,5,6,10,11], provided the crystals are impermeable to the gas.

In a previous paper[17] we showed evidence that gas molecules like carbon dioxide and methane can dissolve and diffuse in PMP crystals formed from the melt. The proposed permeability coefficients for gases through the PMP crystallites in melt-prepared PMP films, shown in *Table 5*, were obtained by extrapolation of experimental data to 100% crystallinity. These values are higher than the permeability coefficients measured for PMP films cast from chloroform (see *Table 5*). The estimated values for transport through PMP crystallites apply only to the melt-prepared crystalline modification (mod. I) and it may be that the crystal modification formed from chloroform and related solvents are not as permeable. Whether the latter assumption is reasonable or not can be resolved in part by evaluation of the volume available for transport in each of the PMP crystalline modifications. Modifications I–III are tetragonal and the volume of the unit cell can be calculated from the unit-cell constants listed in *Table 1*. The crystalline density of mod. I calculated assuming four molecular chains of a (7/2) helix[14–16] is 0.822 g cm^{-3}, in agreement with previously

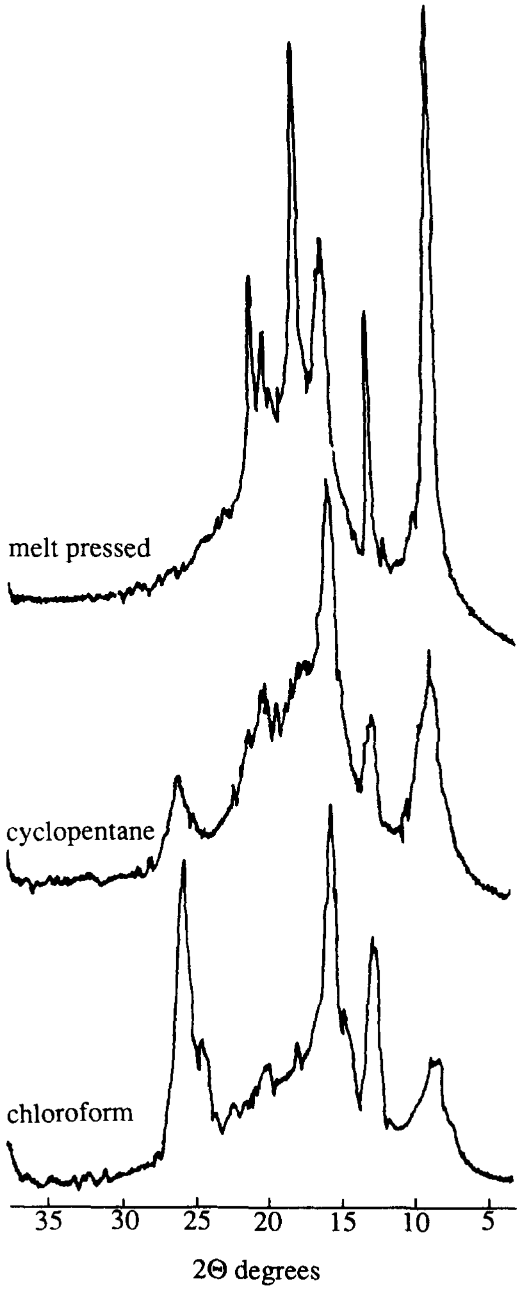

Figure 6 X-ray diffraction patterns of melt-processed PMP and PMP cast from cyclopentane and chloroform

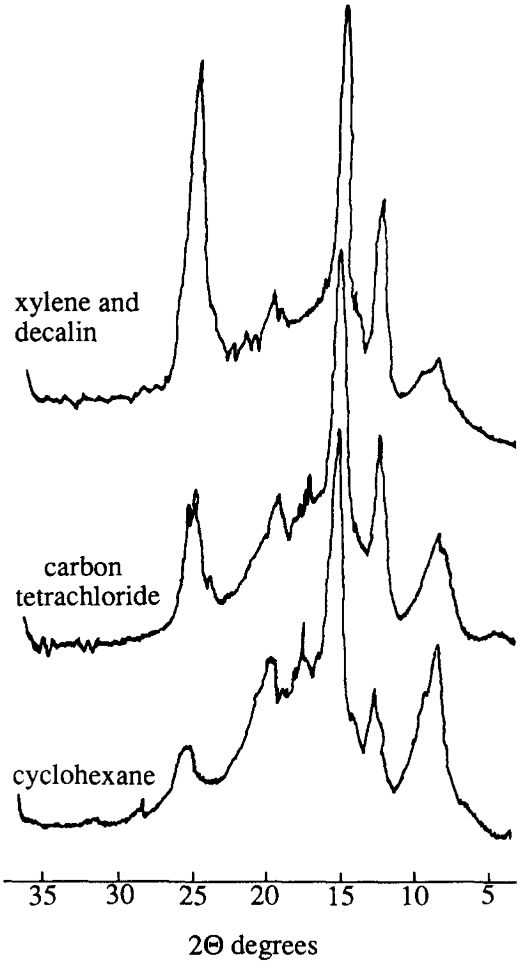

Figure 7 X-ray diffraction patterns of PMP cast from xylene, decalin, carbon tetrachloride and cyclohexane

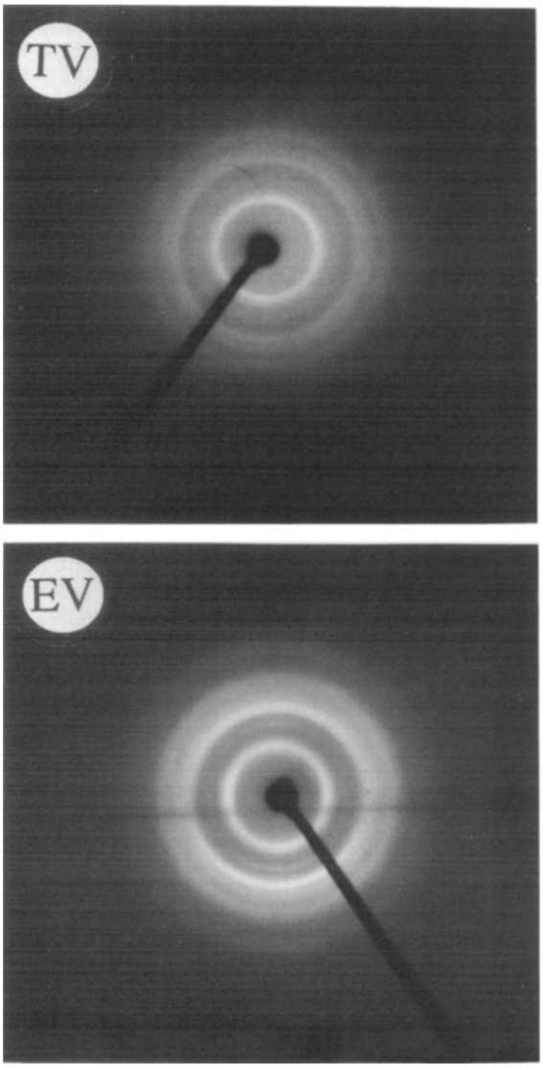

Figure 8 X-ray diffraction photographs of cyclopentane-cast PMP with the X-ray beam normal (through view: TV) and 90° off-normal (edge view: EV) to the film surface

reported values[13,16,36,37]. Modifications II and III have a (4/1) helix[20], which results in calculated crystalline densities of 0.854 and 0.851 g cm^{-3}, respectively. The higher density of crystalline mods. II and III compared to mod. I strongly supports the idea that the former would be significantly less permeable to gases than the latter. Information on the spatial orientation of the polymer chains in the unit cell of the hexagonal mod. IV is not as well documented as for the other modifications. However, the volume of the unit cell can be calculated based on the crystal angles[38] of $\alpha=\beta=90°$ and $\gamma=120°$. The density of the unit cell is found by a trial-and-error estimation of the number of chains and repeat units within the volume that give a reasonable density value. Results of the calculation show that four chains in the unit cell configured such that there are four repeat units per chain (similar to a (4/1) helix) gives a density of 0.784 g cm^{-3}. Other values chosen for the number of chains and molecules give density values that are unreasonably low or high. Thus, it is likely that crystalline mod. IV has a lower density than mods. I, II and III, which correlates with the permeability and sorption results obtained.

The question of whether single-crystal platelets lined up as in *Figure 1a* are formed from chloroform but not cyclopentane can be resolved by experiment. In fact, this was the reason for obtaining the X-ray diffraction photographs shown in *Figures 8* and *9*. Generally, one does not expect a casting procedure that involves no externally applied stress to yield a preferred crystallographic orientation. That, however, is what is seen in *Figure 9* for chloroform-cast films, but to a much lesser

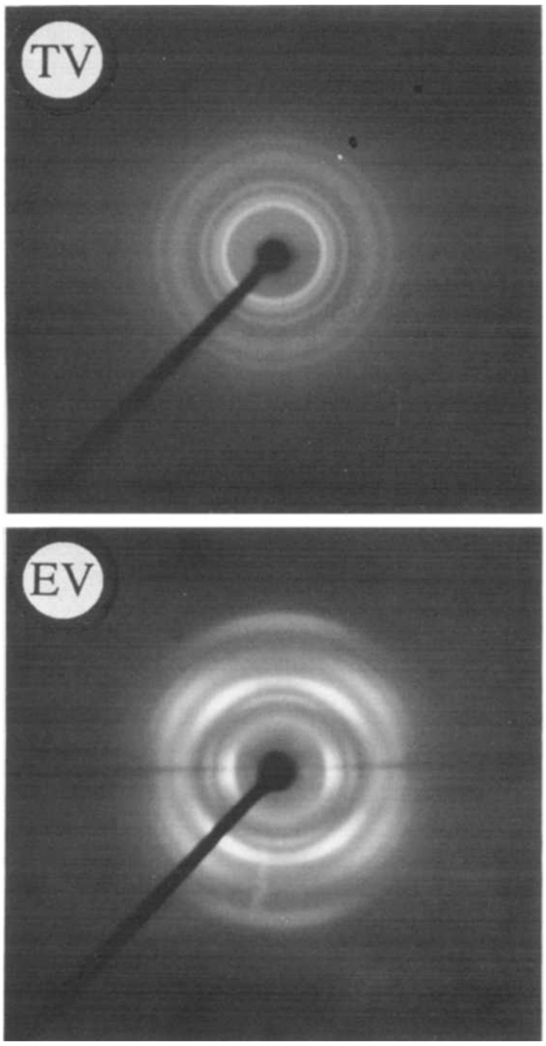

Figure 9 X-ray diffraction photographs of chloroform-cast PMP with the X-ray beam normal (through view: TV) and 90° off-normal (edge view: EV) to the film surface

Table 5 Permeability coefficients for the crystalline phase of PMP and for chloroform-cast PMP

	Permeability[a]	
Gas	Crystal[b]	Chloroform[c]
N_2	2	1.1
O_2	17	5.2
CH_4	4	2.1
H_2	116	33.2
He	88	33.1
CO_2	38	15.0

[a] Units: 10^{-10} cm^3 (STP) cm/(s cm^2 cmHg) at 35°C
[b] Estimated permeability of crystalline phase of melt-processed film from ref. 17
[c] Experimentally measured permeability for chloroform-cast film

extent for cyclopentane-cast films (see in *Figure 8*). One interpretation of *Figure 9* is that these films contain single crystals with their lateral dimensions parallel to the film plane (see EV in *Figure 9*) but that the orientation about the normal axis through the crystals is random within the plane (see TV in *Figure 9*). So we suggest that the gas permeability of cast PMP films depends on the degree to which oriented crystals are formed during the casting process. Some solvents tend to yield structures more like *Figure 1a* because single crystals that can readily orient are formed during film casting, whereas other solvents lead to structures more like *Figure 1b* because of formation of spherulites or single crystals that are not able to orient during film formation.

The annealing response shown in *Figure 2* may reflect a gradual conversion of the oriented crystal structure (*Figure 1a*) to a more disoriented state (*Figure 1b*). To what extent a change in crystalline modification may be involved is simply not known.

The preliminary propane permeation experiments were included here since our earlier work[17] suggested that molecules with a kinetic diameter greater than 4.0 Å would not be able to diffuse through the crystalline mod. I. Propane has a diameter of 4.3 Å[34]. While it is not possible from these experiments to comment on propane diffusion in the crystal, the data do show that propane is less permeable than methane in the chloroform-cast film while the reverse is true for melt-pressed and cyclopentane-cast PMP. Whether this relates to transport in the various crystalline modifications requires further investigation. The permeability of propane relative to methane is also greatly influenced by solubility in addition to molecular size.

The proposal offered above seems to explain most aspects of the unusual permeation behaviour reported here and is consistent with the X-ray and optical characterization of these materials. However, investigations that are more detailed than permitted by the scope of this work are needed to verify and refine all aspects of this phenomenon.

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