Oxygen permeation through films of polypropylene/hydrogenated oligocyclopentadiene blends

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Oxygen permeation through films of isotactic polypropylene (iPP)/hydrogenated oligocyclopentadiene (HOCP) blends was studied as a function of the weight fraction of the two components and temperature. Increasing HOCP content lowers oxygen permeability and diffusivity through the films and increases the glass transition temperature of the polymer blends. Activation energies for permeation and diffusion processes were also measured. Annealing for 2 min at 100°C was shown to completely transform the smectic phase in the α-crystalline form and to induce a marked increase in oxygen permeability and diffusivity, especially in the blends, and a corresponding decrease in the activation parameters.

(**Keywords: oxygen permeation; films; blends**)

INTRODUCTION

Thermal and crystallization behaviour of blends of isotactic polypropylene (iPP) and hydrogenated oligocyclopentadiene (HOCP) has been investigated in previous papers[1,2].

Examination of isothermally crystallized samples by optical microscopy showed that the films were completely filled with spherulites and no segregation of HOCP could be observed. Spherulite growth rate and overall kinetic rate constants were depressed by dilution of iPP with HOCP. This phenomenon is enhanced by increasing concentration of the non-crystallized component and by decreasing undercooling. The glass transition temperature of the blends increased with HOCP concentration, in good agreement with the Fox equation[3]. For a large range of undercooling values, melting temperature was found to increase linearly with the crystallization temperature for both plain iPP and blends. In addition, the equilibrium melting point decreased with HOCP concentration. The Flory–Huggins interaction parameter is negative and close to zero. On the basis of these experimental facts, it was possible to conclude that iPP and HOCP are compatible in the melts[1]. The apparent crystal size was not modified by the presence of HOCP and long period increased as a function of HOCP content, suggesting that HOCP is distributed mainly in the interlamellar regions[2].

In this paper oxygen transport through membranes of iPP/HOCP blends has been studied. Permeation is governed by free volume distribution and mobility of polymer chains in the amorphous phase; it can therefore give important information on the microstructure of polymers. Moreover the possibility of forecasting transport properties of films of polymer blends on the basis of their composition clearly has great practical implications.

EXPERIMENTAL

Materials

Binary blends of iPP (Moplen TS 30S, M_w 300 000, Montedison) and HOCP (Escorez, M_w 630, Esso Chemical) were prepared by mixing the components in an extruder at 240°C. The weight mixing ratios of the two components (iPP/HOCP) were 90/10, 80/20, 70/30 and 50/50. Films were extruded at 280°C and quenched in a cold water stream.

The structure and properties of the quenched and subsequently crystallized (2 min at 100°C) samples were characterized by various techniques.

Density measurements

Densities were measured at 25 ± 0.2°C by floating the samples in water/ethanol mixtures. The mass crystallinity, α_{cr}, of the samples was derived from the measured

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density, ρ_x, solving the following equation system:

$$\begin{aligned} 1/\rho_x &= \alpha_{cr}/\rho_{cr} + \alpha_{am}/\rho_{am} + \alpha_{HOCP}/\rho_{HOCP} \\ \alpha_{cr} &+ \alpha_{am} + \alpha_{HOCP} = 1 \end{aligned} \qquad (1)$$

under the assumption that the crystalline and amorphous components have the ideal values for the perfect crystal, ρ_{cr}, and fully relaxed amorphous material, ρ_{am}, i.e. 0.936 and 0.850 g cm^{-3} respectively[4] and $\rho_{HOCP} = 1.08$ g cm^{-3} (ref. 1).

Wide angle X-ray scattering

The wide angle X-ray scattering (WAXS) data were obtained by a Siemens D-500 diffractometer equipped with a Siemens FK 60-10, 2000 W Cu tube. The samples were mounted on a specimen carrier with a rotational speed of 30 rpm.

Differential scanning calorimetry

A Perkin-Elmer DSC-4/thermal analysis data station system was used. The samples (about 4 mg) were heated from 30°C to 200°C at a scanning rate of 10°C min^{-1}. Glass transition temperatures (T_g) of iPP and the various blends were measured by differential scanning calorimetry (d.s.c.) from −40°C to 80°C.

The crystalline and amorphous weight fractions were calculated from the following relationships:

$$\alpha_{cr} = \Delta H^* / \Delta H_{iPP} \qquad (2)$$

$$\alpha_{am} = (1 - \alpha_{cr}) \qquad (3)$$

where ΔH_{iPP} (44 cal g^{-1}) is the heat of melting per gram of 100% crystalline iPP and ΔH^* is the apparent enthalpy of melting of plain iPP and/or the blends under investigation.

Amorphous and crystalline fractions and experimental T_g values are reported in *Tables 1* and *2*. T_g values are consistent with the Fox equation[3], considering the overall weight fractions.

Table 1 Densities (ρ), crystalline and amorphous weight fractions (α_{cr} and α_{am}, respectively) and glass transition temperatures (T_g) of quenched films of plain iPP and iPP/HOCP blends

iPP/HOCP (weight fraction)	ρ (g cm^{-3})	α_{cr}[a]	α_{cr}[b]	α_{am}	T_g (K)
100/0	0.894	0.49	0.43	0.51	259.0
90/10	0.910	0.45	0.36	0.55	265.0
80/20	0.924	0.41	0.33	0.59	270.0
70/30	0.937	0.32	0.29	0.68	278.0
50/50	0.955	0.04	0.21	0.96	292.0
0/100	1.080	0.0		1.0	338.2

[a] From density measurements
[b] From d.s.c. measurements

Table 2 Densities (ρ), and crystalline and amorphous weight fractions (α_{cr} and α_{am}, respectively) of annealed films of plain iPP and iPP/HOCP blends

iPP/HOCP (weight fraction)	ρ (g cm^{-3})	α_{cr}	α_{am}
100/0	0.902	0.63	0.37
90/10	0.914	0.53	0.47
80/20	0.928	0.45	0.55
70/30	0.943	0.38	0.62
50/50	0.967	0.16	0.84

Permeation measurements

The apparatus used for the measurement of transport properties of oxygen through films of polymer blends has been described in detail in a previous paper[5]. The system employs a differential technique[6]. The copper cell consists of two compartments separated by the membrane under study; a steady flow of oxygen passes in the upstream compartment, while the gas permeating through the film is collected by a stream of helium in the downstream part and carried to the analytical equipment.

Membrane areas were 15.9 cm^2. Constant temperature conditions were set up by immersing the whole apparatus in a thermostatted bath. Permeability measurements were carried out in the temperature range from −10°C to 50°C with a tolerance of ±0.1°C.

Oxygen concentrations in the carrier gas were determined by means of a Perkin-Elmer 990 gas chromatograph, using thermal conductivity detection and 3 mm columns, 20 cm long, filled with 60/80 molecular sieve 5A, at 60°C and 25 ml min^{-1} flow rate.

Prior to transport experiments, helium was allowed to flow through both chambers of the diffusional cell for about 12 h, in order to condition the film and to clean the cell from any contaminant. Then oxygen was introduced in the upstream compartment at a constant flux of 332 ± 52 ml min^{-1}, corresponding to approximately 60 ± 9 compartment volume changes per minute and time recording started from that moment. Helium was kept flowing in the downstream compartment at a constant flux of 31 ± 3 ml min^{-1}, corresponding to approximately 7.8 ± 0.8 volume changes per minute.

Permeabilities were measured from permeated oxygen flux values under steady state conditions (Φ_{ss}), while diffusion coefficients were obtained from:

$$D = l^2 / 6\theta_L \qquad (4)$$

where l is the thickness of the film and θ_L is the 'time lag'[6] calculated from:

$$\theta_L = \int_0^{ss} (1 - \Phi/\Phi_{ss})\,dt \qquad (5)$$

RESULTS AND DISCUSSION

iPP may present three different crystalline structures, the monoclinic form being the most common. A liquid crystalline form, usually called 'smectic', can be obtained when iPP, as well as iPP/HOCP blends, is rapidly quenched from the melt[7]. The presence of the smectic form is revealed by two broad peaks in WAXS scans. This pattern suggests that the smectic structure is an intermediate state, not completely ordered, but more ordered than amorphous iPP. Plain iPP quenched films show only the diffraction peaks typical of the α-crystalline form, while quenched films of iPP/HOCP blends are characterized by two peaks at $2\theta = 14.8°$ and $2\theta = 21.5°$, corresponding to the smectic form. An increase in HOCP content lowers the diffraction pattern of the α-crystalline form, and it finally disappears completely in the 50/50 film. On the contrary, as shown in *Figure 1*, the smectic form seems to increase with respect to the crystalline form as HOCP content increases, becoming dominant in the 50/50 film. If the quenched films undergo subsequent annealing the smectic portion of the WAXS scan disappears.

Inspection of d.s.c. thermograms of the quenched films, reported in *Figure 2*, shows that an exothermic peak, centred at about 95°C and extending from 60°C to 110°C, is observed only in the blends. This small but broad peak may be attributed to the transformation from smectic to monoclinic crystal structure; however, a quantitative evaluation of the smectic phase is prevented by the fact that the enthalpy of the smectic–crystal transition is not known. As described above, annealing of the films at temperatures up to 100°C decreases the area of the exothermic peak; for long annealing times and higher temperatures the peak is practically absent, as shown in *Figure 2*. On the other hand, thermally treated samples present a small endothermic transition, having a maximum which increases with annealing temperature and displaces itself until it finally coincides with the melting peak ($\sim 160°C$)[8].

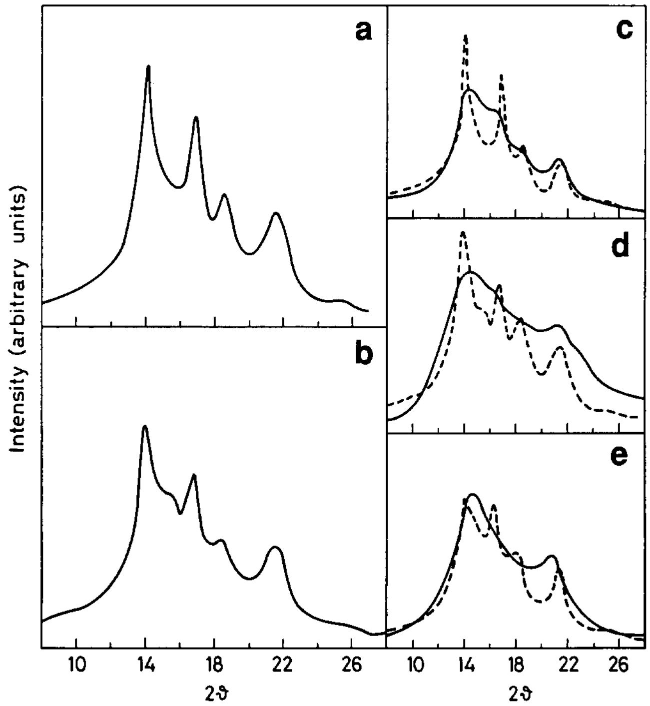

Figure 1 Wide angle X-ray diffraction of pure iPP and iPP/HOCP blends. Solid line: quenched films; broken line: annealed films. Weight fractions of iPP/HOCP blends: a, 100/0; b, 90/10; c, 80/20; d, 70/30; e, 50/50

Specific experiments on the films studied here have shown that annealing of the samples for 2 min at 100°C is sufficient to completely transform the smectic phase in the α-crystalline form. iPP and iPP/HOCP blends subjected to the above thermal treatment are indicated as annealed films in the following text.

Table 1 presents density values, crystallinity fractions (α_{cr}) obtained by density measurements as well as by d.s.c. on the basis of ΔH_f (melting enthalpy at melting point), and finally glass transition temperatures (T_g) for quenched iPP and iPP/HOCP blend films. Crystalline fractions determined through densitometry and through d.s.c. are in broad agreement, with the exception of the 50/50 iPP/HOCP blend where the observed discrepancy is likely to be due to the crystallization of the sample during d.s.c.

Amorphous and crystalline fractions of annealed films obtained by density measurements (see equation (1)) are reported in *Table 2*.

Oxygen transport properties

Apparent oxygen permeabilities, *P*, of all the films studied were measured following the method described in Experimental. These phenomenological values are the most important as far as practical applications are concerned. Permeation may be regarded as a thermally activated process, expressed by an equation of the Arrhenius type, i.e.

$$P = P_0 \exp(-E_P/RT) \qquad (6)$$

where E_P is the activation energy of the transport of oxygen in the films. An analogous relationship is found for diffusion coefficients.

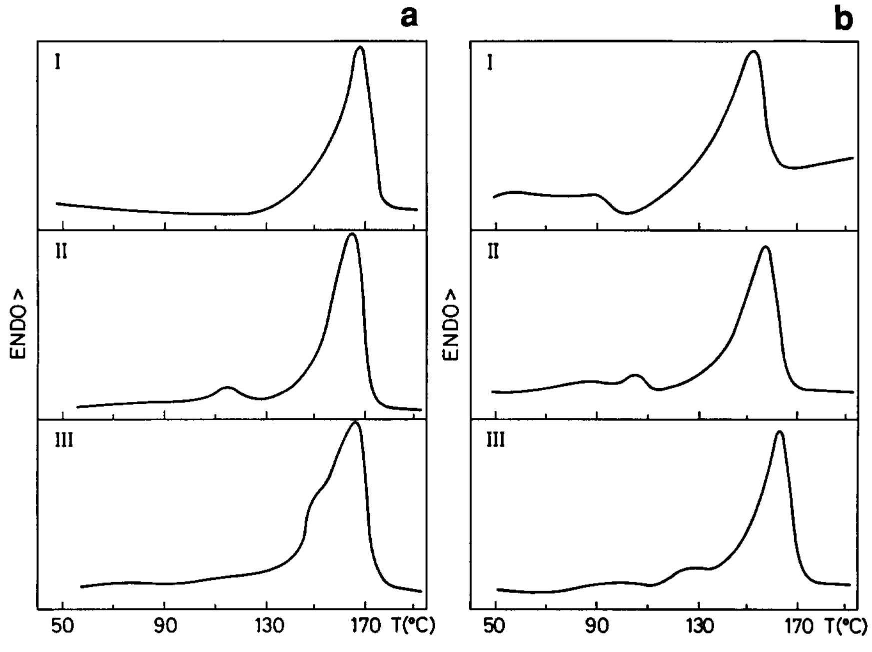

Figure 2 D.s.c. thermograms of (a) pure iPP and (b) iPP/HOCP blends. I, Quenched films; II, films annealed for 2 min at 100°C; IIIa, film annealed for 2 min at 135°C (plain iPP); IIIb, film annealed for 2 min at 110°C (50/50 iPP/HOCP blends)

Table 3 Oxygen permeabilities, P through plain iPP and iPP/HOCP blends at different temperatures

	$P \times 10^{10}$ [cm^3(STP) cm cm^{-2} cmHg^{-1} s^{-1}] in iPP/HOCP blends (weight fraction)									
	100/0		90/10		80/20		70/30		50/50	
T (K)	q[a]	a[a]	q	a	q	a	q	a	q	a
263.2	0.12	0.15		–		–		–		–
268.2	0.18	0.21	0.10	0.16		–		–		–
273.2	0.25	0.29	0.15	0.21	0.13	0.45		–		–
278.2	0.34	0.39	0.21	0.29	0.19	0.56	0.18	0.28		–
283.2	0.47	0.52	0.29	0.39	0.25	0.69	0.25	0.35		–
303.2	1.49	1.51	0.96	1.12	0.80	1.46	0.76	0.80	1.13	1.18
310.2		–		–		–		–	1.49	1.45
317.2		–		–		–		–	1.94	1.77
323.2	4.11	3.83	2.76	2.85	2.17	2.84	2.03	1.66	2.42	2.09

[a] q = quenched films; a = annealed films

Table 4 Activation parameters of oxygen permeability, E_P, and diffusivity, E_D in films of plain iPP and IPP/HOCP blends

iPP/HOCP (weight fraction)	E_P (kcal mol^{-1})		E_D (kcal mol^{-1})	
	q[a]	a[a]	q	a
100/0	9.8 ± 0.5	9.1 ± 0.5	13.0 ± 0.6	11.9 ± 0.8
90/10	10.3 ± 0.6	9.1 ± 0.5	13.0 ± 0.5	9.1 ± 0.6
80/20	9.8 ± 0.6	6.4 ± 0.4	11.7 ± 0.6	9.3 ± 0.3
70/30	9.6 ± 0.8	7.1 ± 0.6	10.5 ± 0.6	8.7 ± 0.5
50/50	7.4 ± 0.3	5.6 ± 0.2	7.7 ± 0.2	3.2 ± 0.1

[a] q = quenched films; a = annealed films

The experimental oxygen permeabilities of quenched and annealed films of iPP and iPP/HOCP blends in the temperature range 260–323 K, are collected in *Table 3*; E_P data are reported in *Table 4*.

Inspection of the data shows that oxygen permeability decreases with increasing HOCP content in the blend samples, while E_P is markedly affected by the thermal history of the samples, being lowered by annealing.

In the case of 70/30 iPP/HOCP film, some measurements were carried out below T_g. As expected, the activation energy measured under these conditions is smaller than that measured at higher temperatures (*Figure 3*).

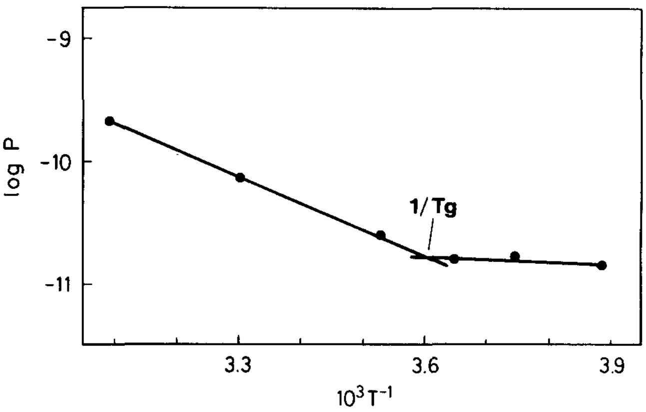

Figure 3 Arrhenius plot of oxygen permeabilities, P [cm^3 (STP) cm cm^{-2} s^{-1} cmHg^{-1}], through iPP/HOCP (70/30) quenched films. For $T < T_g$ $E_P = 1.7$ kcal mol^{-1}; for $T > T_g$ $E_P = 9.6$ kcal mol^{-1}, where T = absolute temperature

From permeation experiments together with steady state permeabilities, diffusivity values, D, can also be obtained. Diffusivities of the various films are reported in *Table 5*; activation energies of the diffusional process, E_D, are shown in *Table 4*.

Table 5 Oxygen diffusivities, D, in films of plain iPP and iPP/HOCP blends at different temperatures

	$D \times 10^8$ (cm^2 s^{-1}) in iPP/HOCP blends (weight fraction)									
	100/0		90/10		80/20		70/30		50/50	
T (K)	q[a]	a[a]	q	a	q	a	q	a	q	a
263.2	0.011	0.021		–		–		–		–
268.2	0.018	0.032	0.010	0.021		–		–		–
273.2	0.028	0.048	0.015	0.029	0.010	0.031		–		–
278.2	0.042	0.072	0.023	0.039	0.015	0.042	0.010	0.013		–
283.2	0.064	0.105	0.035	0.052	0.022	0.057	0.016	0.020		–
303.2	0.29	0.42	0.16	0.15	0.086	0.17	0.11	0.076	1.23	1.67
310.2		–		–		–		–	1.65	1.88
317.2		–		–		–		–	2.18	2.11
323.2	1.11	1.43	0.62	0.39	0.28	0.44	0.57	0.25	2.73	2.31

[a] q = quenched films; a = annealed films

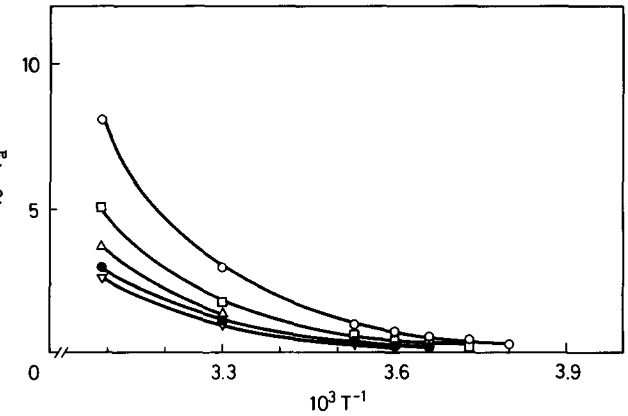

Figure 4 Effective oxygen permeability, P_a [cm^3 (STP) cm cm^{-2} s^{-1} $cmHg^{-1}$], of quenched films of plain iPP and iPP/HOCP blends as a function of reciprocal absolute temperature, T^{-1}. Weight fractions of iPP/HOCP blends: ○, 100/0; □, 90/10; △, 80/20; ●, 70/30; ▽, 50/50

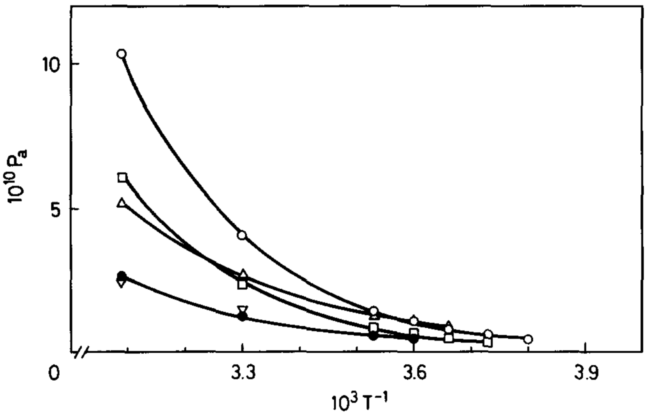

Figure 5 Effective oxygen permeability, P_a [cm^3 (STP) cm cm^{-2} s^{-1} $cmHg^{-1}$], of annealed films of plain iPP and iPP/HOCP blends as a function of reciprocal absolute temperature, T^{-1}. Weight fractions of iPP/HOCP blends: ○, 100/0; □, 90/10; △, 80/20; ●, 70/30; ▽, 50/50

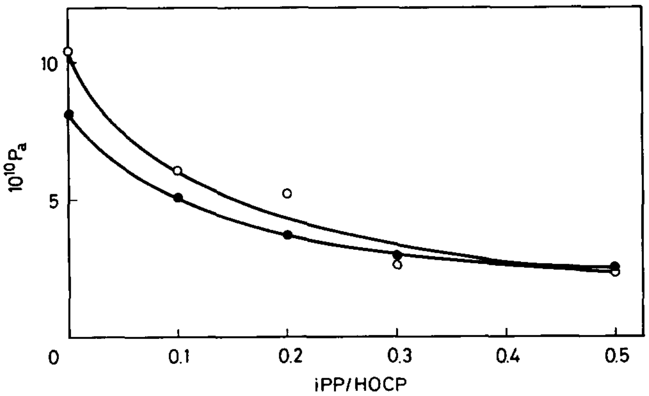

Figure 6 Effective oxygen permeabilities, P_a [cm^3 (STP) cm cm^{-2} s^{-1} $cmHg^{-1}$], of annealed (○) and quenched (●) films as a function of membrane composition (iPP/HOCP: weight fraction of the two components) at 323.2 K

It is well known that gas permeation in polymers takes place only in the amorphous part, while crystalline regions act as excluded volumes for the sorption process and as effective impermeable barriers for diffusion. As a consequence, permeabilities are generally found to increase as α_{cr} decreases. As a first approximation, the permeability per unit of the amorphous component, P_a, can be calculated according to the following relationship:

$$P_a = P/\alpha_{am} \tag{7}$$

which has been found to be valid for several cases[9]. P_a values are represented in graphic form in *Figures 4* and *5*. In the present case, on the contrary, addition of HOCP to iPP gives rise to markedly lower crystallinities, but also lower permeabilities, as shown by inspection of *Tables 3* and *5*, as well as *Figure 6*; the effect is enhanced if the effective permeabilities, P_a, are considered. Analogously the increasing content of the non-crystallizable component, HOCP, decreases oxygen diffusivities. This behaviour is in line with the increase in T_g brought about by increasing the HOCP fraction in the polymer films; in fact higher T_g values necessarily correspond to a decrease in free volume with a parallel loss in the frequency of polymer segmental motions of iPP chains. HOCP has substantially an antiplasticizing effect and produces a restriction in penetrant mobility.

On the other hand, thermal treatment carried out as described above increases both permeation and diffusion coefficients, even if annealing brings about an increase in crystallinity (see *Tables 2, 3* and *5*). The effect of annealing is more important for the blends than for plain iPP and is especially marked in the case of 80/20 iPP/HOCP blend: for example at 273.2 K this blend shows a permeability and diffusivity increase of about 260% and 210%, respectively, while the corresponding values for plain iPP are 59% and 71%. As shown in *Table 4*, annealing markedly lowers permeation and diffusion activation energies. This experimental behaviour may be attributed to an increase in microporosity as a consequence of an increase in the crystalline fraction or of the transformation of the smectic phase into a crystalline phase[10].

REFERENCES

1 Martuscelli, E., Silvestre, C., Canetti, M., De Lalla, C., Bonfatti, A. and Seves, A. *Makromol. Chem.* 1989, **190**, 2615
2 Martuscelli, E., Canetti, M. and Seves, A. *Polymer* 1989, **30**, 304
3 Fox, T. G. *Bull. Am. Phys. Soc.* 1956, **2**, 123
4 Van Krevelen, D. W. 'Properties of Polymers', Elsevier, New York, 1976
5 Marcandalli, B., Selli, E.,Tacchi, R., Bellobono, I. R. and Leidi, G. *Desalination* 1984, **51**, 113
6 Felder, R. M. *J. Membrane Sci.* 1978, **3**, 15
7 Hsu, C. C., Geil, P. H., Miyayi, H. and Asai, K. *J. Polym. Sci. B* 1986, **24**, 2379
8 Fichera, A. and Zanetti, R. *Makromol. Chem.* 1975, **176**, 1885
9 Myers, A. W., Rogers, C. E., Stannett, V. and Szwarc, M. *TAPPI* 1958, **41**, 716
10 Vicini, L., Sadocco, P., Canetti, M., Galli, R. and Seves, A. *Acta Polym.* 1984, **35**, 588