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The barrier properties of polyethylene terephthalate to mixtures of oxygen, carbon dioxide and nitrogen

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Abstract

The diffusion and solubility of oxygen, nitrogen and carbon dioxide have been studied in amorphous and biaxially oriented films of polyethylene terephthalate (PET). To measure the sorption and desorption of each gas simultaneously in cases where mixtures of gases were studied, a mass spectrometer was used as a detector. It was found that the solubility and diffusion of nitrogen in PET were markedly affected by the presence of the other gases, oxygen and carbon dioxide with differences in detail between results for the amorphous and biaxially oriented films. It is of particular interest that the presence of oxygen reduces the solubility and increases the diffusivity of nitrogen.

Keywords: Permeability; Mixed Gases; PET

1. Introduction

The gas barrier properties of polymer films is a subject of considerable commercial importance, which also provides an interesting challenge to polymer scientists. The pioneering research of Barrer [1] was expanded and developed by many subsequent workers, for example Michaels and Bixler [2], Hopfenberg and co-workers [3], Rogers [4], Paul and Koros [5].

The present publication stems from two key motivations. First, there is the interest in the influence on the gas barrier properties of the physical structure of polymer films, especially molecular orientation. This has been exemplified in a number of previous publications [6,7] showing that major differences in permeability can be related to changes in structure, especially molecular orientation. Secondly, there is the recognition that, in many practical instances, there is simultaneous diffusion of several different gas species.

In this paper, the diffusion and solubility of two-gas and three-gas mixtures in polyethylene terephthalate films has been studied. Oxygen, nitrogen and carbon dioxide were chosen as the gases, and two very different film structures examined: an amorphous unoriented film, and a biaxially-oriented film which closely resembles commercially available products.

We find that the diffusion and solubility of the components of the mixed gases vary in a non-trivial manner as compared with the individual gases. Similar effects have been observed in polystyrene (PS) and poly(methylmethacrylate) for oxygen diffusion [8]. Here a ‘low’ pressure domain (<500 Torr) is observed. In this region the diffusion coefficient of oxygen increases with increasing pressure of added gas.

2. Theory

The flux **F** (actually an intensity) of flow of one substance in a mixture is defined as the amount of that substance in unit time passing through a surface of unit area normal to the flow direction. This is proportional to the concentration gradient in that direction, and may be written in general as:

$$\mathbf{F} = -D\nabla c, \qquad (1)$$

where c is the concentration of the penetrant, and D is the diffusion coefficient (diffusivity), which has dimensions L^2T^{-1}. This is Fick’s First Law.

The case of a thin sheet is one-dimensional, for which the change in concentration with time at a distance x into the sheet is given by

$$\frac{\partial c}{\partial t} = \frac{\partial F_x}{\partial x},$$

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which, from Eq. (1), gives

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right). \tag{2}$$

If D is independent of concentration (which is usually true in polymers above their glass transition temperature) and position in the sample (it is homogeneous), this becomes

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}, \tag{3}$$

which is Fick's Second Law, and such diffusion is termed 'Fickian'. In the present work, the experiment is 'single-sided', in which the penetrant is introduced to only one side of the sample; then the boundary conditions for an absorption run are such that the solution to Eq. (3) is [9]

$$\Delta F = \left[(4/\sqrt{\pi})X\sum_{n=1}^{\infty}\exp(-n^2X^2)\right]\Delta F_\infty \quad \text{for } n \text{ odd}, \tag{4}$$

where ΔF is the flux above background level, ΔF_∞ is the final steady-state flux above background, $X^2 = l^2/(4Dt)$, where l is the sample thickness, and t is the time after the gas was admitted. This solution has a characteristic sigmoidal shape.

The concentration c of dissolved gas is related to its partial pressure p by the expression

$$c = Sp, \tag{5}$$

which obeys Henry's law when S is independent of p.

The dynamic flow method [10] was the method used. The test film is mounted between an input gas line and an output line. After evacuating both gas lines, the test gas (mixture) is introduced at time $t = t_0$ at a known pressure to the input line, and the gas(es) permeating through the sample to the output line is (are) removed continuously, the flow rate being recorded as a function of time. This is the sorption experiment. Eventually equilibrium is reached, when the flow rate becomes constant. The gas (mixture) is then removed from the input line, and the flow rate continuously monitored at the output until the flow ceases. This is the desorption experiment. The parameters P and D, and hence S, can be measured from each experiment.

3. Experimental

3.1. PET samples

Two sheets of PET have been examined. The first was biaxially oriented (i.e. balanced draw ratio in two directions) of about 4 × 4 'Melinex'™ sheet. It was called 'ML'. The second was amorphous (clear) unoriented PET sheet called 'VU'. The samples to be used in the mass spectrometer apparatus were discs of diameter 50 mm cut from these sheets. The biaxial sample, ML2, had a thickness of 56 ± 1 μm; the unoriented one, VU1, had a thickness of 204 ± 1 μm.

3.2. Test gases

The test gases and gas mixtures were obtained from BOC Ltd. The pure gases were oxygen, carbon dioxide and 'white spot' nitrogen, and were quoted as 99.7% pure. Most mixtures of gases in the required concentrations were also obtained from BOC Ltd, with certified mixtures of about the same percentage purity. Some of the earlier two-gas mixtures were prepared in the desired concentrations in the apparatus. Gas proportions (in %) will be expressed in the order $O_2/CO_2/N_2$ in this paper.

3.3. Measurement method

In order to measure the sorption and desorption of more than one gas simultaneously, a mass spectrometer was used as the detector. The mass spectrometer vacuum apparatus has been described before [11], so that only a summary is given here. The mass spectrometer itself was a Spectramass Dataquad Model DAQ-100 quadrupole type, which was capable of measuring up to 16 gases simultaneously. The Dataquad control unit was interfaced with an Elonex PC-320X computer, with a program which collected the data and stored it onto disc for subsequent analysis. The vacuum arrangement is shown schematically in Fig. 1. The input (low vacuum) side was connected to a large buffer gas reservoir, into which the gas (mixture) could be introduced at any total pressure up to about 1050 mbar, measured to an accuracy of 1 mbar, and via valves to a rotary pump for gas removal. The high vacuum side was pumped continuously by an Edwards 'Diffstak'® Model 63/150M oil diffusion pump with an ultimate vacuum of 2×10^{-8} Torr. The mass spectrometer head was positioned between the sample cell and the diffusion pump. If the diffusion pump speed was great enough to ensure a constant pumping rate to the volume between it and the sample, the flux of gas through that volume will be proportional to the pressure of gas at the head.

The relation between gas flux and pressure was calibrated for each gas by the use of a pinhole of known area instead of the sample, and found to be linear. The number of gas molecules striking unit area per second is given by

$$N = \tfrac{1}{4}n\bar{c}, \tag{6}$$

where n is the number density of the effusing gas, and $\bar{c}$ is the mean speed of the molecules. Then, applying simple gas laws, this becomes

$$E_a = \frac{p}{p_0}\sqrt{\frac{kT}{2\pi m}}, \tag{7}$$

where E_a is the effusion rate as volume at atmospheric

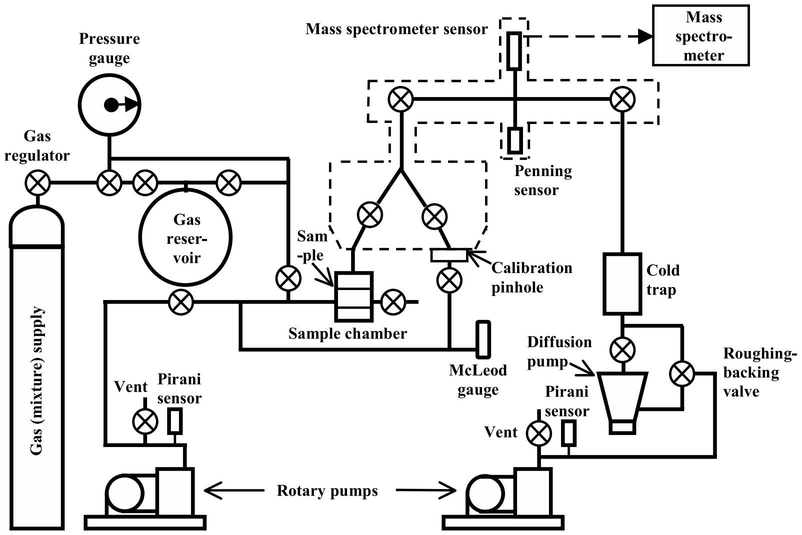

Fig. 1. The gas diffusion vacuum apparatus. The upper surface of the sample and the components enclosed in dashed lines comprise the high-vacuum section. The crossed circles represent valves.

pressure, per unit area of pinhole per second, p is the input pressure (measured by an Edwards 'Vacustat' McLeod gauge), p_0 is atmospheric pressure (760 Torr, 1013.25 mbar), T is the gas temperature, m is the mass of the gas molecule, and k is Boltzmann's constant. From the definition of permeability as $P = \Delta F_\infty l/\Delta p$, where Δp is the partial pressure difference across the sample, P from this apparatus becomes

$$P = \frac{\Delta Q_\infty A_\mathrm{h}}{G p_0 A}\sqrt{\frac{kT}{2\pi m}}\frac{l}{\Delta p}, \tag{8}$$

where ΔQ_∞ is the steady-state partial pressure of the gas at the mass spectrometer head (Torr), $A_\mathrm{h} = (7.78 \pm 0.12) \times 10^{-6}\ \mathrm{cm}^2$ is the area of the pinhole, G is the gradient of a calibration graph of mass spectrometer pressure (Torr) versus McLeod pressure (Torr), and A the area of the sample in its cell (9.9 cm^2). A calibration was performed before and after each run, and was later found not to vary from run to run; the optimum calibration consant was then taken to be the mean of all calibrations done thus far. The sample itself was maintained at 25 °C.

The procedure was to pump down both sides of the apparatus until all permeants that were absorbed in the sample had fully desorbed and the high vacuum side stabilised at a background level of about 1×10^{-7} Torr (measured on a Penning gauge), then data collection was initiated, and the test gas at known pressure was introduced to the sample from the buffer reservoir at a known time. Data collection was ended when a steady state was reached; then the desorption experiment was started after restarting data collection by evacuating the gas from the sample, and again collection terminated when steady-state background levels were regained. The buffer total pressure was monitored during the absorption runs, so that the results could be corrected for any decrease in this pressure during the run. This was particularly important for carbon dioxide, where the permeability is relatively high. In order to ensure that the technique was giving the correct answers, preliminary runs had been made with oxygen on undrawn Rigidex 006-60 linear polyethylene as used by Holden et al. [6]; the values for the barrier properties agreed satisfactorily with those in that paper.

3.4. Data analysis

Permeabilities were calculated from Eq. (8), the units being $10^{-12}\ \mathrm{cm}^3$ (STP) $\mathrm{cm}^{-2}\ \mathrm{s}^{-1}$ cm (cm Hg)$^{-1}$ (l in cm;

Table 1
Rates of diffusion (diffusion coefficients, D, in units of $10^{-9}\ \mathrm{cm}^2\ \mathrm{s}^{-1}$) of the three pure gases at 25 °C in the samples

Gas	Amorphous VU1	Drawn ML2	Ratio ML2/VU1
Oxygen	4.843 ± 0.367	3.302 ± 0.194	0.682 ± 0.065
Carbon dioxide	0.836 ± 0.027	0.684 ± 0.022	0.818 ± 0.037
Nitrogen	0.688 ± 0.040	0.963 ± 0.030	1.400 ± 0.092

Table 2
Solubility S in units of $10^{-3}\ \mathrm{cm}^3$ (at STP) cm^{-3} (1 atm)$^{-1}$ (upper), and No. of gas molecules per repeat unit (lower) of the three pure gases at 25 °C in the samples

Gas	Amorphous VU1	Drawn ML2	Ratio ML2/VU1
S in $10^{-3}\ \mathrm{cm}^3$ (at STP) cm^{-3} (1 atm)$^{-1}$			
Oxygen	146 ± 11	92 ± 4	0.629 ± 0.057
Carbon dioxide	3340 ± 230	2000 ± 140	0.599 ± 0.058
Nitrogen	191 ± 31	52 ± 4	0.273 ± 0.049
S (number of gas molecules per repeat unit) $\times 10^{-3}$			
Oxygen	0.93 ± 0.07	0.59 ± 0.03	
Carbon dioxide	21.40 ± 1.50	12.80 ± 0.90	
Nitrogen	1.22 ± 0.20	0.34 ± 0.02	

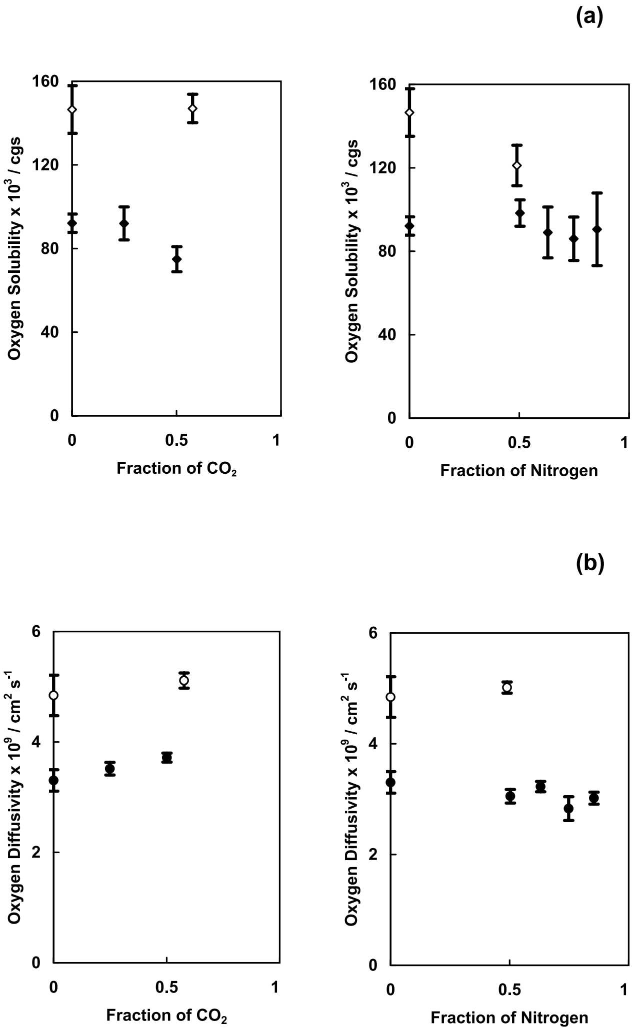

Fig. 2. The effects of carbon dioxide or nitrogen on (a) oxygen solubility and (b) diffusion coefficient (diffusivity) in two-gas mixtures. Open symbols refer to the amorphous unoriented PET, solid ones to Melinex 4 × 4 biaxially-drawn film. The temperature of the samples was 25 °C. The (cgs) units for solubility are 10^{-3} cm^3(STP) cm^{-3} (atm)$^{-1}$.

Δp in cm Hg). For diffusivities, Eq. (4) was fitted to the experimental data using the Microsoft spreadsheet Excel. Three parameters were fitted: D, ΔF_∞, and the time of admission of the gas. It was found that six exponentials were sufficient for the present samples (i in Eq. (4) $n^2 = 1, 9, \ldots 121$). A desorption experiment was then carried out after the steady-state condition of the absorption run had been reached; the fitted equation has 1 minus the sum of the terms in the square brackets in Eq. (4), and similar parameters fitted. The units of D are 10^{-9} cm^2 s^{-1}. The solubility was calculated from $S = 76P/D$, so that its units are 10^{-3} cm^3(STP) cm^{-3} (atm)$^{-1}$.

The errors (uncertainties) in the results are the following: (i) in the sample thickness l and its non-uniformity; (ii) in the exposed sample area A; (iii) in effects due to sample temperature variation; (iv) in the purity, composition and partial pressures of the gases (negligible); (v) in the goodness of fit to the theoretical curves; (vi) in the run-to-run variability; and (vii), for P and S only, in the area A_h of the pinhole (1.5%), and from the variability in measurements of the calibration constant G. For each gas, there was found to be no correlation between the run-to-run variability and the variability in G, so that the weighted mean of all the calibration runs was taken to be the best value for G for that gas. It was also found that (vi) was usually the largest factor, and the mean result from several runs were weighted by the mean square deviation of the fitted curve from the data points (related to (v)), the standard error of that mean being taken as the random error of that result. If total uncertainties are required, an additional ~2% from (i)–(iv) should be added to those in D, and ~6% (mainly from 5% in G) to P and S. Whenever the fit to the data points was poor (i.e. the behaviour of gas flux did not accord with Eq. (4)), the value of D thus obtained was excluded from the calculation of the mean D; this appeared to occur mainly for desorption runs for nitrogen.

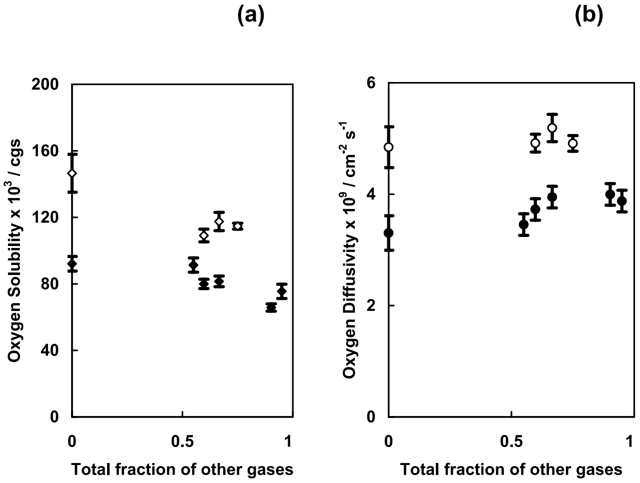

Fig. 3. The effects of carbon dioxide and nitrogen on (a) oxygen solubility and (b) diffusion coefficient in three-gas mixtures. The proportions of gases % O_2/% CO_2/% N_2 away from the y axis (100% O_2) from left to right, are: amorphous unoriented PET 40:10:50, 33:34:33, 25:25:50; Melinex 4 × 4 PET film 45:5:50, 40:10:50, 33:34:33, 10:40:50, 5:45:50. Symbols etc. as in Fig. 2.

There was a further possible source of uncertainty for the nitrogen results. In the mass spectrum of carbon dioxide, calling the height of mass $m/e = M = 44$ 100%, there is a peak at $M = 28$ due to the CO fragment that is produced in the ionisation chamber of the mass spectrometer. The height of this peak was found to be 15% of the $M = 44$ peak. This coincides with the $M = 28$ peak of nitrogen, so whenever both gases were being used together in a mixture it was necessary to subtract 15% of the carbon dioxide data point-by-point from the nitrogen data to remove this contribution. There were no overlap problems for oxygen ($M = 32$) or for the $M = 44$ carbon dioxide peak itself.

Also to be noted is that there was always a contribution from H_2O to the total pressure. The mass spectrum of H_2O is 23% $M = 17$ per 100% $M = 18$, and was found to be very stable. The $M = 17$ peak was recorded simultaneously with

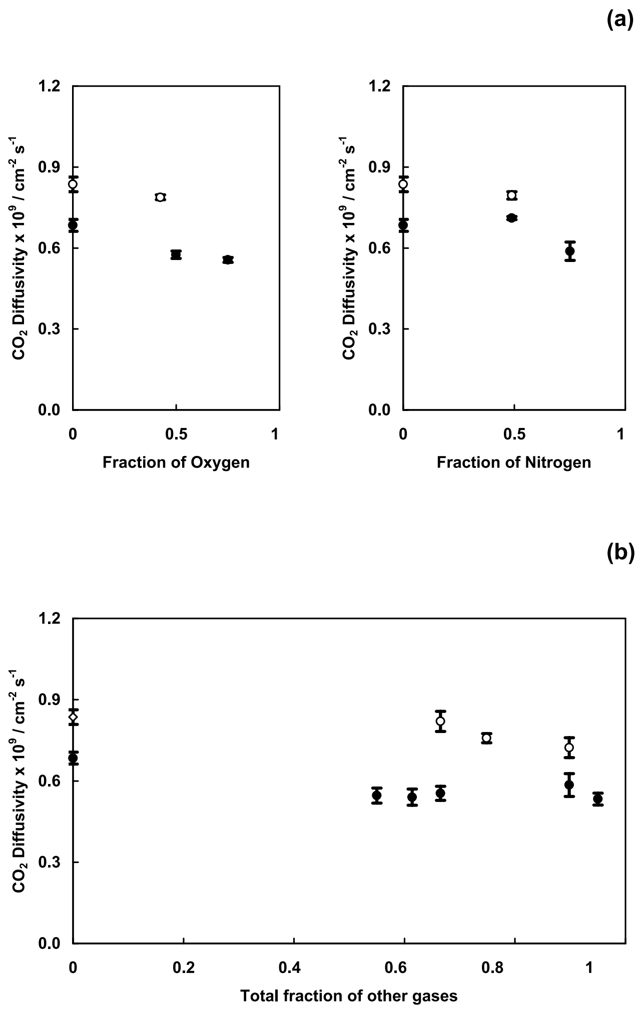

Fig. 4. The effects of oxygen and nitrogen on the diffusion coefficient of carbon dioxide: (a) oxygen or nitrogen in two-gas mixtures; (b) three-gas mixtures, with gas proportions, for amorphous unoriented PET 33:34:33, 25:25:50, 40:10:50; Melinex 4 × 4 PET film 5:45:50, 10:40:50, 33:34:33, 40:10:50, 45:5:50. Symbols etc. as in Fig. 2.

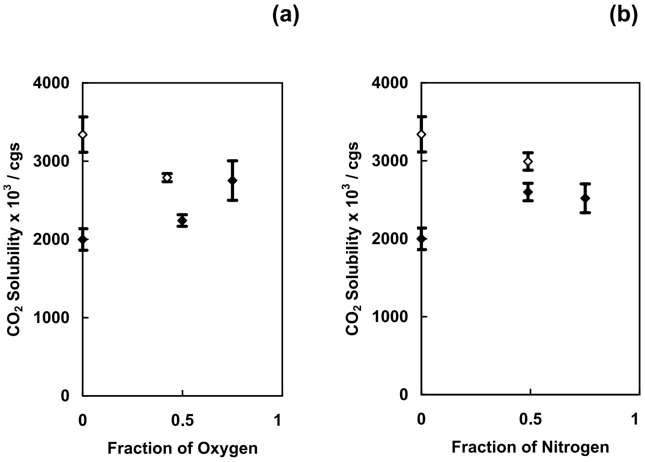

Fig. 5. The effects of (a) oxygen or (b) nitrogen on the solubility of carbon dioxide, in two-gas mixtures. Symbols etc. as in Fig. 2.

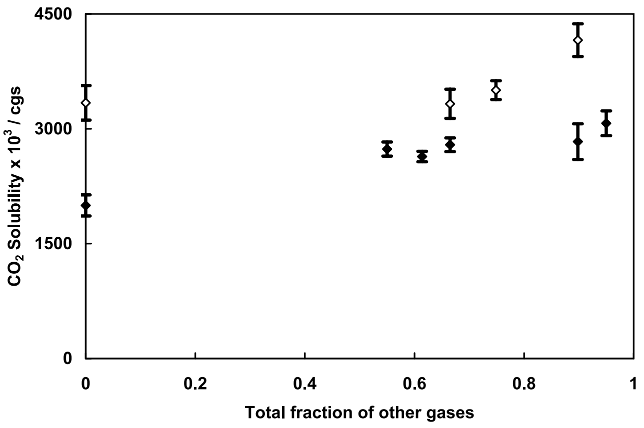

Fig. 6. The effects of oxygen and nitrogen on the solubility of carbon dioxide in three-gas mixtures, with gas proportions as in Fig. 4(b). Symbols etc. as in Fig. 2.

the gas peaks, to monitor this contribution; it was often the largest contribution, but varied little and slowly with time. Such H_2O contamination of the vacuum apparatus is extremely difficult to remove by baking without damaging the sample, so it was left alone.

A further mass peak was also recorded: this was $M = 40$ from argon in the air (0.934% by volume near sea level [12]), and was used to monitor any contamination from air leaks.

4. Results

4.1. General features

A useful starting point for the consideration of the diffusion and solubility of the three gases studied is a comparison of the values of D and S at room temperature for the pure gases at 25 °C. These results are shown in Tables 1 and 2 for the amorphous PET film VU1 and the biaxially oriented film ML2. Two very striking features are immediately apparent for both films. First, the diffusion

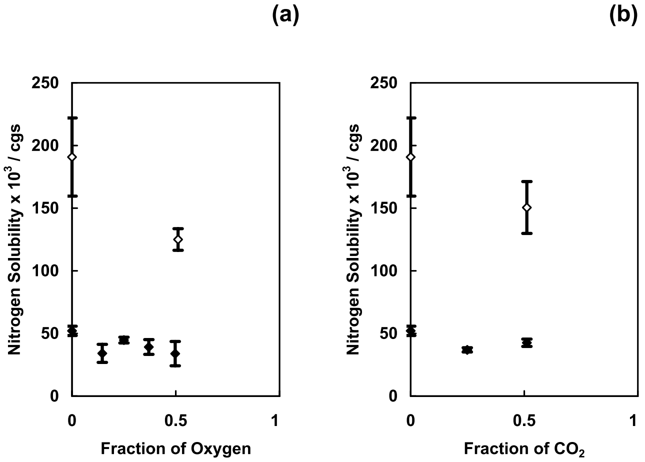

Fig. 7. The effects of (a) oxygen or (b) carbon dioxide on the solubility of nitrogen, in two-gas mixtures. Symbols etc. as in Fig. 2.

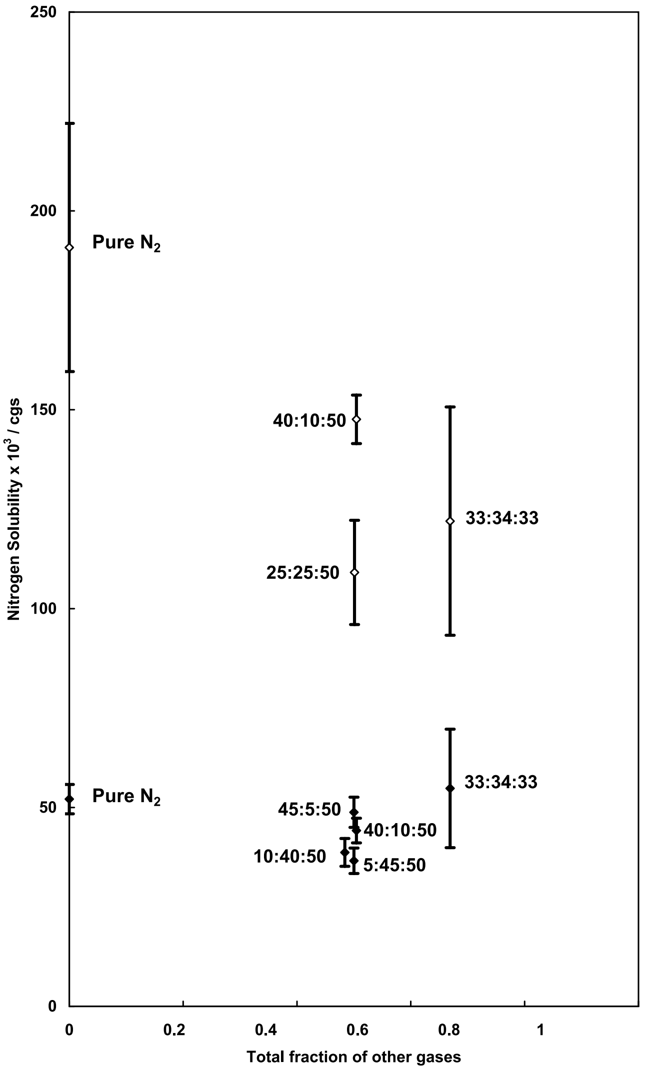

Fig. 8. The effects of oxygen and carbon dioxide on the solubility of nitrogen in three-gas mixtures, with gas proportions. Symbols etc. as in Fig. 2. % gases in order O_2:O_2:N_2.

coefficient for oxygen is considerably greater than those for nitrogen or carbon dioxide, which are very similar. The higher diffusion coefficient for oxygen than nitrogen has been found in other polymers, such as polyethylene, [2,10, 11,13], PET [10,13,14], (poly(oxymethylene) [10], poly (vinyl chloride) [13], poly(tetrafluoroethylene) [13], poly (ethyl methacrylate) [10], many rubbers [10,13], oriented polypropylene [15] and poly (4-vinylpyridene) film [16]. Secondly, the solubility of carbon dioxide is more than one order of magnitude greater than that of oxygen and nitrogen (as in Ref. [17]), the last being quite similar. The solubilities are also expressed in Table 2 in terms of the number of gas molecules per repeat unit.

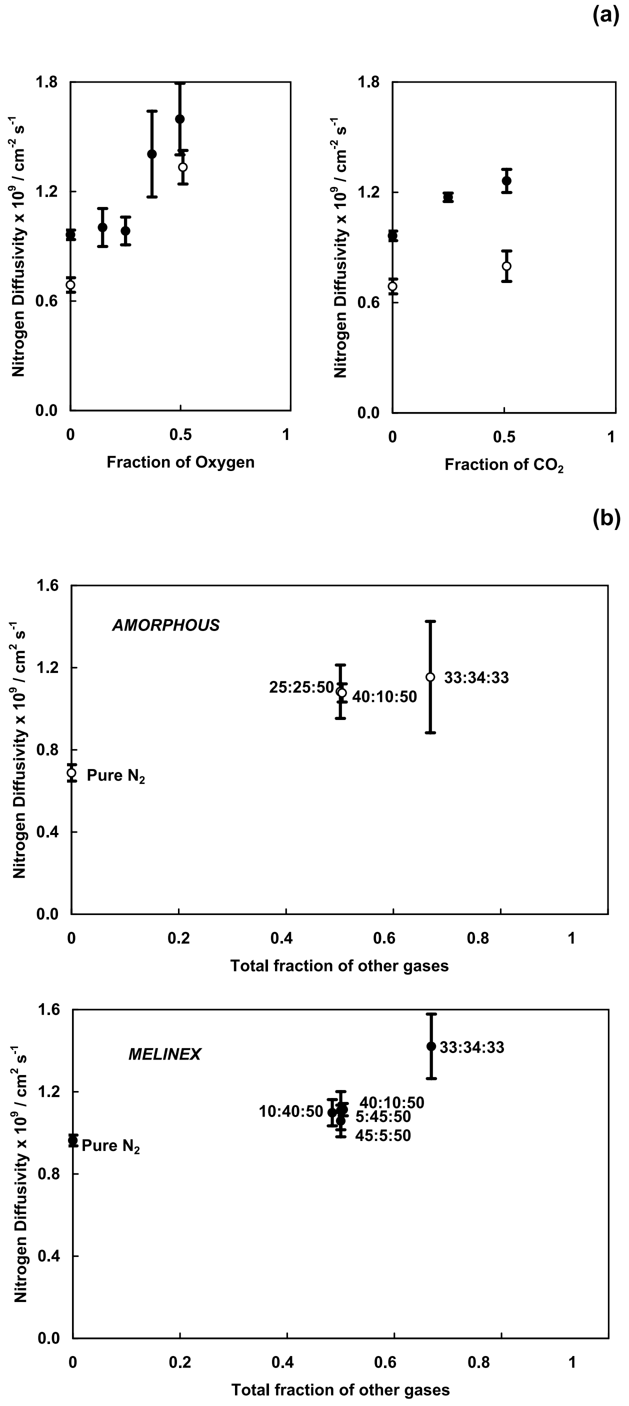

Fig. 9. The effects of oxygen or carbon dioxide on the diffusion coefficient of nitrogen (a) in two-gas mixtures, (b) in three-gas mixtures, in which upper is amorphous unoriented PET; lower is Melinex 4 × 4 PET film. Symbols etc. as in Fig. 2.

It is worth noting here that the thickness of the biaxially oriented film ML2 had been found to have increased by (12 ± 2)% immediately after an absorption run with gas partial pressures of 510 mb carbon dioxide and 514 mb nitrogen. In view of the relative solubilities of the two gases, this would suggest that one atmosphere of carbon dioxide would cause an increase of about 24% in the thickness of this film. No change in sample diameter could be measured. Also it is known that carbon dioxide plasticizes PET (its T_g is depressed) [18].

Previous research [17,19–21] has shown that the permeability $P = DS$ of oxygen in PET is reduced by

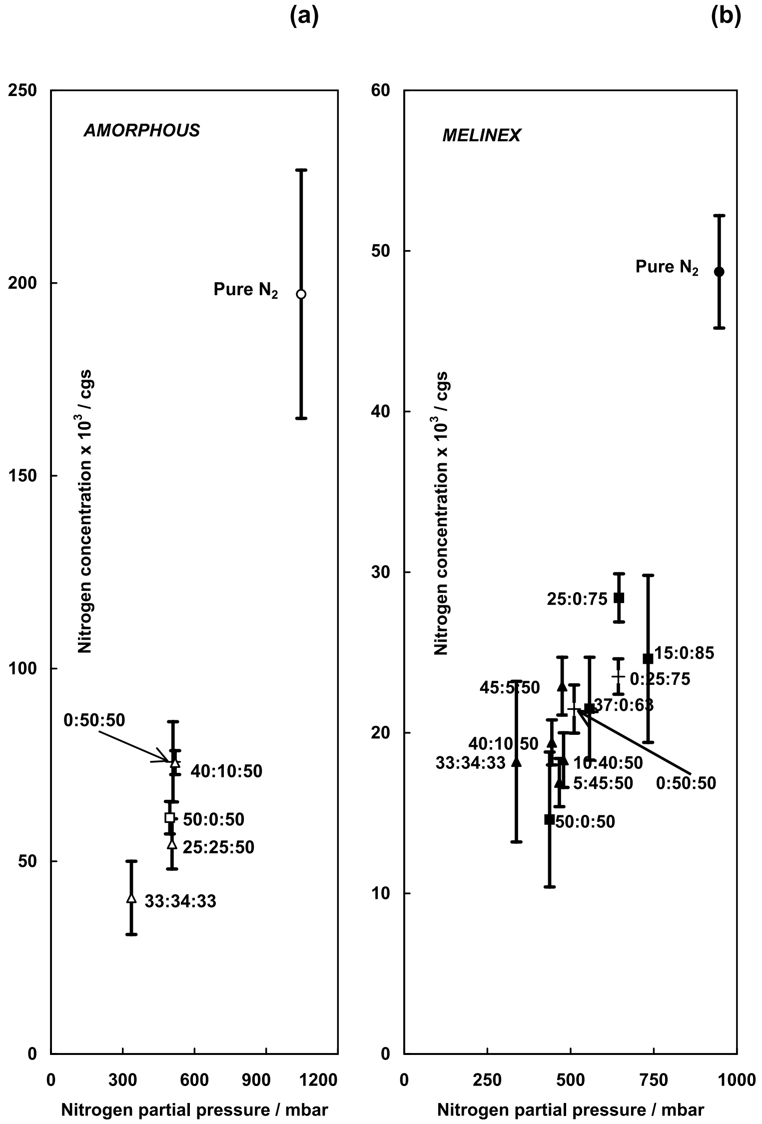

Fig. 10. Nitrogen concentration in 10^{-3} cm^3(STP) cm^{-3} vs. nitrogen partial pressure in the presence of the other gases (a) for amorphous unoriented PET; (b) for Melinex 4 × 4 PET film. In this and the next two figures, ' + ' represents two gases, no oxygen; squares represent two gases, no carbon dioxide; diamonds represent two gases, no nitrogen; triangles represent three-gas mixtures; and circles the pure gas.

crystallisation and by orientation. The present results are consistent with this, and suggest that both *D* and *S* are reduced by the increase in crystallinity and molecular orientation of the oriented film, compared with the amorphous film. Similar reductions are observed for the solubilities of nitrogen and carbon dioxide (as in Ref. [17]) and for the diffusion coefficient of carbon dioxide, but it is surprising that the diffusion coefficient of nitrogen shows a contrary effect. We will see, however, that there are other unanticipated results for the diffusion behaviour of nitrogen.

5. The diffusion and solubilities of gases in gas mixtures

5.1. Oxygen

Because of the very rapid diffusion of oxygen compared to nitrogen and carbon dioxide, it is perhaps not surprising that the oxygen solubility and diffusion are only slightly affected by the presence of nitrogen or carbon dioxide. In general, there is a slight decrease in the solubility in the case of the two-gas mixtures (Fig. 2(a)), and very little effect on the diffusion (Fig. 2(b)). The three-gas mixtures show the decrease in solubility more clearly (Fig. 3(a)), with the diffusion little affected: only a slight increase with increased concentration of the other gases in the case of the oriented film only (Fig. 3(b)), which could be attributed to the effect of CO_2 (Fig. 2(b)).

It is perhaps surprising, in view of the comparatively high concentration of CO_2, that the solubility and diffusion of oxygen are so little affected by it.

5.2. Carbon dioxide

In the case of two-gas mixtures, the diffusion of carbon

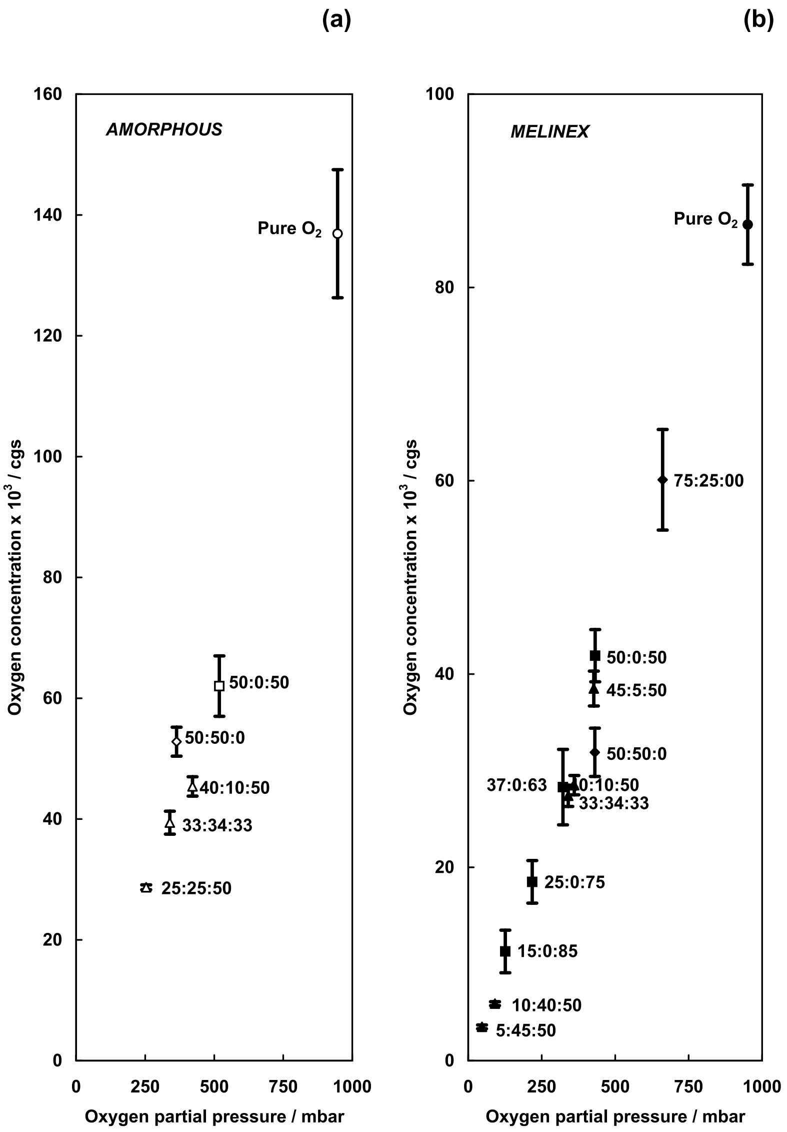

Fig. 11. Oxygen concentration in 10^{-3} cm^3(STP) cm^{-3} vs. oxygen partial pressure in the presence of the other gases (a) for amorphous unoriented PET; (b) for Melinex 4 × 4 PET film. Symbols as in Fig. 10.

dioxide is almost unaffected by nitrogen and oxygen in the amorphous film, and slightly decreased by oxygen content in the oriented crystalline film (Fig. 4(a)). As was the case for oxygen, the effects are less clear-cut for three-gas mixtures, where slight decreases in diffusion are observed for increased concentration of the other gases (Fig. 4(b)). It appears from the two-gas mixture results that this result may be due to the effect of oxygen concentration, not nitrogen concentration.

In contrast to the rather small effects in the case of diffusion, the solubility of carbon dioxide is significantly decreased by oxygen concentration in the amorphous film, but increased by oxygen concentration in the oriented film, in the case of the two-gas mixtures (Fig. 5(a)). The results for the effect of nitrogen are somewhat similar: the carbon dioxide solubility is increased with increasing nitrogen concentration in the oriented film, but probably little affected in the amorphous film (Fig. 5(b)). Results for three-gas mixtures show that the carbon dioxide solubility shows a slight increase with increasing concentration of the other gases for both amorphous and oriented film (Fig. 6).

5.3. Nitrogen

The solubility and diffusion of nitrogen are significantly affected by the presence of the other gases. For example, in two-gas mixtures, in both films, its solubility decreases with increasing oxygen content (Fig. 7(a)) and carbon dioxide content (Fig. 7(b)); and three-gas mixtures show a similar pattern (Fig. 8).

Also, the nitrogen diffusion is markedly increased by the presence of the other gases, for both two-gas and three-gas mixtures (Fig. 9(a) and (b)). The faster diffusion of oxygen could be preventing nitrogen molecules being absorbed in

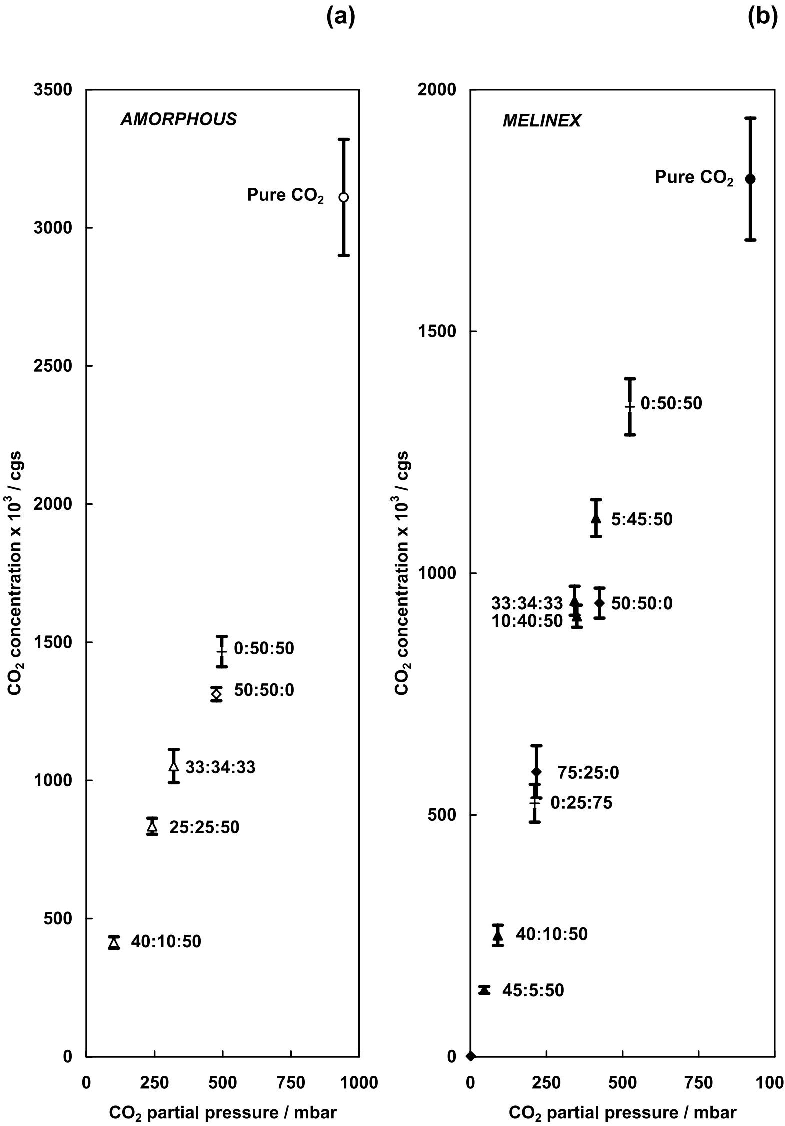

Fig. 12. Carbon dioxide concentration in 10^{-3} cm^3(STP) cm^{-3} vs. carbon dioxide partial pressure in the presence of the other gases (a) for amorphous unoriented PET; (b) for Melinex 4 × 4 PET film. Symbols as in Fig. 10.

sites already occupied by oxygen (Fig. 7(a)), and so allowing the nitrogen to diffuse through more rapidly by decreasing the tortuosity. In addition, the high absorption of carbon dioxide could be causing structural changes in the polymer [18], opening the structure up, and thus permitting a higher diffusion rate for nitrogen (Fig. 9).

5.4. Gas concentrations

Plots of gas concentration versus partial pressure of gas in question show that Henry's law is obeyed to a good approximation for oxygen (Fig. 11) and to a lesser degree for nitrogen (Fig. 10) and carbon dioxide (Fig. 12). The present work focused on 50% mixtures of nitrogen (~500 mbar partial pressure) in particular, and the results for this nitrogen concentration are brought out more clearly in Fig. 13. It can be seen that both oxygen and carbon dioxide slightly depress the take-up of nitrogen in both films, and that the effect of each of these gases is much the same (the fitted straight lines have gradients which are not significantly different from zero, and supported by Figs. 7 and 8, which show similar rates of decrease of solubility with oxygen and carbon dioxide).

6. Discussion

The most striking results are the effects of the other gases, oxygen and carbon dioxide, on the solubility and diffusion of nitrogen in PET, with some differences in detail between the amorphous film and the crystalline biaxially oriented film. It appears reasonable to regard the effects of oxygen and carbon dioxide as being different in origin. Carbon dioxide swells the structure, producing larger free

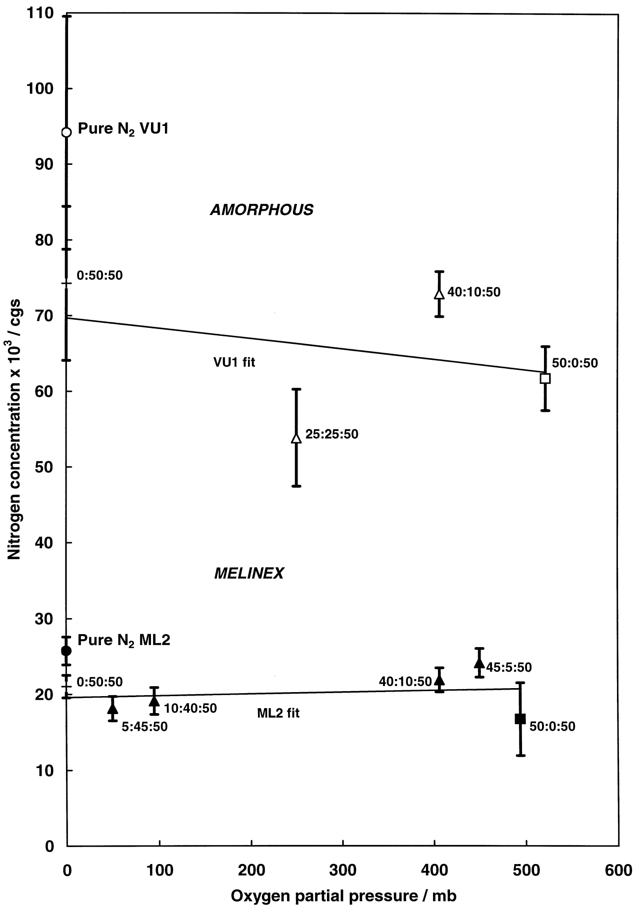

Fig. 13. Effect of oxygen on the concentration of nitrogen in the two samples, with straight lines fitted to the points by least squares. Symbols as in Fig. 10.

volume for dissolving nitrogen. The effect is very much greater in the drawn film and it is possible to speculate that this is due to the reduction in the degree of the close packing between the planes of the PET molecules so that the free volume rises to a similar value to that of the amorphous film; hence the rise in the nitrogen diffusion rate to a value much greater than that for the amorphous film. It is perhaps surprising that the solubility of nitrogen in both films is somewhat reduced by the presence of carbon dioxide.

The effect of oxygen on the nitrogen solubility and diffusion appears to be a separate issue and essentially independent of the effect of carbon dioxide on the PET structure. The rapid diffusion of oxygen into the PET may lead to oxygen occupying sites that would otherwise be occupied by nitrogen, or oxygen may affect the nitrogen sites making nitrogen location at that site less favourable. Therefore, nitrogen has fewer sites, at any given temperature, upon which it can be localised. This would result in more frequent hopping between sites. Thus the oxygen modification:occupancy of the nitrogen sites would have two effects; it would reduce the solubility and it would increase the diffusivity, as we have observed experimentally. Contrary to the results of Poulsen et al. [8] we do not see a increase in the diffusivity with added nitrogen and only a small increase with added CO_2.

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References

[1] Barrer RM. Trans Faraday Soc 1939;35:628.
[2] Michaels AS, Bixler HJ. J Polym Sci 1961;50:393 and 413.
[3] Berens AR, Hopfenberg HB. J Membr Sci 1982;10:283.
[4] Rogers CE. In: Comyn J, editor. Polymer permeability. London: Elsevier Applied Science; 1985. ISBN 0-85334-322-5.
[5] Paul DR, Koros WJ. J Polym Sci, Polym Phys Ed 1976;14:675.
[6] Holden PS, Orchard GAJ, Ward IM. J Polym Sci, Polym Phys Ed 1985;23:709.
[7] Taraiya AK, Orchard GAJ, Ward IM. Plastics, Rubber and Composites, Proc Appl 1993;19:273.
[8] Poulsen L, Ogilby PR. J Phys Chem A 2000;104:2573.
[9] Pasternak RA, Schimscheimer JF, Heller J. J Polym Sci, Part A-2 1970;8:467.
[10] Crank J, Park GS. Diffusion in polymers. London: Academic Press; 1968.
[11] Webb JA, Bower DI, Ward IM, Cardew PT. J Polym Sci, Part B: Polym Phys 1993;31:743.
[12] Donnelly RJ. In: Anderson H, editor. A physicist's desk reference—the second edition of physics Vade mecam. New York: American Institute of Physics; 1989. p. 199.
[13] Paul DR, DiBenedetto AT. J Polym Sci C 1965;10:17.
[14] Michaels AS, Vieth WR, Barrie JA. J Appl Phys 1963;34:13.
[15] Nörenberg H, Miyamoto T, Fukugami N, Tsukahara Y, Smith GDW, Briggs GAD. Vacuum 1999;53:313.
[16] Shieh JJ, Chung TS. J Polym Sci, Part B: Polym Phys 1999;7:2851.
[17] Michaels AS, Vieth WR, Barrie JA. J Appl Phys 1963;34:1.
[18] Chiou JS, Barlow JW, Paul DR. J Appl Polym Sci 1985;30:2633.
[19] Slee JA, Orchard GAJ, Bower DI, Ward IM. J Polym Sci, Part B: Polym Phys 1989;27:71.
[20] Orchard GAJ, Spiby P, Ward IM. J Polym Sci, Part B: Polym Phys 1990;28:603.
[21] Dhoot SN, Freeman BD, Stewart ME, Hill AJ. J Polym Sci, Part B: Polym Phys 2001;39:1160.