Survey on Transport Properties of Liquids, Vapors, and Gases in Biodegradable Poly(3-hydroxybutyrate) (PHB)

O. MIGUEL, M. J. FERNANDEZ-BERRIDI, J. J. IRUIN

Departamento de Ciencia y Tecnologia de Polimeros, Facultad de Quimica, Universidad del Pais Vasco. P.O. Box 1072. 20080 San Sebastian, Spain

ABSTRACT: The transport properties of carbon dioxide, water, and different organic solvents in bacterial poly(3-hydroxybutyrate)(PHB) at 30°C were investigated. CO_2 sorption was measured by the gravimetric method using a recording microbalance at subatmospheric pressures. Results were adequately interpreted in terms of Henry's law. Organic solvent and water permeabilities for both vapors and liquids were measured using a gravimetric cell. The data were interpreted in different terms depending on the units in which permeability was measured. Most of the solvent–polymer systems showed the typical time-lag plot, but in liquid permeation experiments, some anomalous behaviors were observed, with a transient period of rapid permeation at the beginning of the experiment before reaching the steady state. The transport properties of PHB were compared with those of other polymers, either from synthetic or biodegradable origin. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 1849–1859, 1997

Key words: transport properties; permeability; biodegradable polymers; PHB

INTRODUCTION

Plastic packaging waste is a growing environmental problem partially due to the widespread use of nondegradable synthetic polymers. Therefore, it would be of great interest to develop a polymer which could break down in the environment without leaving any toxic products behind.

Poly(3-hydroxybutyrate)(PHB) is a biosynthetic and biodegradable thermoplastic, produced by many bacteria as an energy-storage product from renewable resources. It is a highly crystalline polymer with a melting point of about 450 K, degrading quickly after such a temperature. This, as well as the fact of having a rather brittle behavior, has prevented its early widespread use as a commodity thermoplastic.[1]

Some different solutions have been proposed to overcome these drawbacks. One of them is the development of copolymers of 3-hydroxybutyrate with 3-hydroxyvalerate to reduce the melting point. This facilitates the processing and makes the polymer tougher.[2] Another alternative is blending. PHB has proven to be miscible with many other polymers[3] like PEO, PVAc, PECH, PVOH, and PVPh. Research about PHB blends is being done in our laboratory at the moment.[4]

PHB is fully biodegradable and recyclable, both in terms of material recycling (like other conventional thermoplastics) and organic recycling by composting.[5] Furthermore, the rate of biodegradation in moist air is negligible, and, therefore, its shelf life should be acceptable in most end uses. All these features make polyhydroxyalkanoates especially suitable for plastic packaging.

Despite these promising expectations, very little has been published on the transport properties of PHB: Razumovskii et al.[6] studied the sorption and diffusion of water and some common organic

solvents, Franz[7] studied the permeation of flavor compounds through PHB, Yoon et al.[8] used chloroform sorption to characterize the miscibility of PHB and PEO, and work about semipermeable porous membranes of PHB was also done by Ben Aoumar et al.[9] In addition, some authors have mentioned PHB gas barrier properties in relation to PVC, PP, and PET[10–12] without giving any quantitative information.

In this context, the aim of the present article was to provide a preliminary insight into the transport properties of organic liquids and vapors, water, and carbon dioxide through PHB. We studied the permeation of vapors and liquids using a gravimetric cell,[13] whereas the CO_2 sorption was followed with a Cahn microbalance.

EXPERIMENTAL

Materials

Bacterial PHB was purchased from Aldrich in powder form. Films of uniform thickness (about 20 microns), measured with an induction magnetic-type meter (Duo-Check St-10), were slowly cast from 3% chloroform solutions onto a flat PTFE surface. The CO_2 employed in the sorption experiments was of a 99.995% purity, and the solvents used for the permeation tests were of a purity higher than 99%.

Differential Scanning Calorimetry

Crystallinity determinations were performed in a Perkin-Elmer DSC-2C calorimeter, equipped with a TADS (thermal analysis data station), using indium as a calibration reference. Samples of all the films tested were heated from 320 to 480 K at 20 K min^{-1}, and crystallinity was determined from the area of the melting peak.

Gas Sorption Experiments

CO_2 sorption was performed gravimetrically by means of a Cahn D-200 microbalance, with a sensitivity of 0.1 μg. The sorption chamber was thermostated at 30°C. Equilibrium sorption runs were done at pressures of 200, 400, 600, 800, and 1000 milibar. Before each run, the sample was outgassed until no change in weight was achieved.

Table I Characteristics of the Films Used in CO_2 Sorption Experiments

Sample	Crystallinity % (DSC)	Thickness (μm)	Sample Weight (mg)
A	66.8	25.2	21.1
B	59.9	18.4	40.5

The description of the PHB samples used in CO_2 sorption experiments appears in Table I.

Permeation Experiments

Organic solvent and water permeabilities were measured using a PTFE gravimetric cell, which is basically a small container partially filled with liquid, with a polymeric membrane sealing its top. The solvent vapor inside the cell permeates the polymeric membrane and evaporates into the air. This process is reflected as a reduction in the overall weight of the cell. In the present study, a computer-connected Sartorius analytical balance with a sensitivity of 10^{-5} g was used. If the gravimetric cell is placed downward, the liquid comes in contact with the membrane so that liquid permeation can be measured. A similar cell has been described elsewhere.[13]

All the results shown in the present work represent the average of two or three independent experimental measurements. The original films were submitted to a thermal treatment of 3 weeks at 65°C under a vacuum to allow total solvent removal and crystallization. The average crystallinity of the samples used in these experiments was 67%, as determined by DSC.

RESULTS AND DISCUSSION

Carbon Dioxide Sorption and Difussion

Using the Cahn electrobalance, the CO_2 solubility in PHB films (C_0) was calculated from the weight gain after sorption equilibrium was reached, by means of the relation

$$C_0 = \frac{22414 M_\infty}{MW_{gas} V_{plm}} \qquad (1)$$

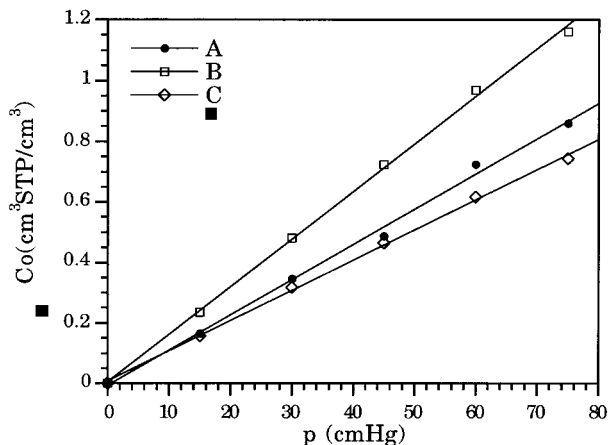where M_∞ is the penetrant equilibrium mass in grams; MW_{gas}, the penetrant molecular mass;

Figure 1 CO_2 sorption isotherms at 30°C in PHB films.

Figure 2 CO_2 diffusion coefficients at 30°C in PHB films.

and V_{plm}, the polymer volume in cm^3; C_0 is in cm^3 STP/cm^3.

Sorption isotherms for CO_2 in PHB films at 30°C are shown in Figure 1. The sample A isotherm lies under that of sample B, as one could expect from its lower amorphous content, assuming that no sorption takes place in the crystalline regions of the polymer. The linearity of these isotherms indicates that the solubility of CO_2 in PHB is within the Henry's law limit under the conditions of this study. The solubility coefficient, S (cm^3 STP/cm^3 cmHg), can be described by Henry's Law as

$$C_0 = Sp \qquad (2)$$

Therefore, S can be obtained from the slope of a C_0 vs. p plot.

Under the experimental conditions used in this study, the fractional amount M_t/M_∞ of the penetrant absorbed by the polymer film at time t is given by[14]

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \left[\frac{8}{(2n+1)^2 \pi^2} \right]$$

$$\times \exp\left[\frac{-D(2n+1)^2 \pi^2 t}{4l^2} \right] \qquad (3)$$

where M_t is the weight gain at time t; n, an integer; l, the film thickness; and D, the diffusion coefficient in cm^2/s. For long times, eq. (3) can be approximated by
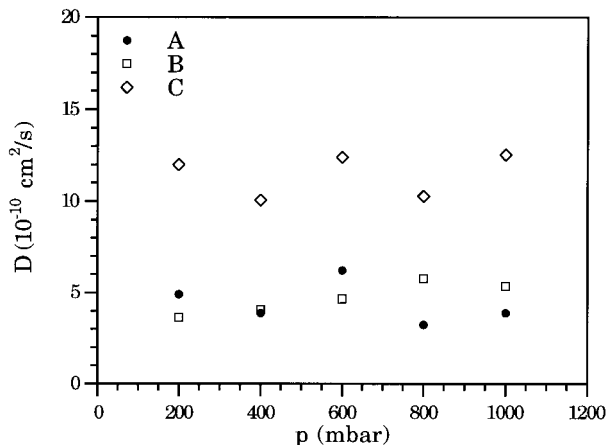
$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \exp\left[\frac{-D\pi^2}{l^2} t \right] \qquad (4)$$

and D can be calculated by an adequate plot of sorption data. Diffusion coefficients obtained from the linear portions of $\ln(1 - M_t/M_\infty)$ vs. time representations are shown in Figure 2. The diffusion coefficient appears to be concentration independent within the range studied here, without significative differences between samples A and B. Since Henry's law applies in the case of CO_2 in PHB, at least for the pressure range studied here, and given that the diffusion coefficient seems to be concentration independent, the permeability can be calculated from[14]

$$P = DS \qquad (5)$$

All the CO_2 sorption results are summarized in Table II.

Water and Organic Vapor Permeation Experiments

Vapor permeation experiments were carried out using the gravimetric cell. In accordance with

Table II Results of the CO_2 Sorption Experiments with Different PHB Films at 30°C

Sample	D (10^{-10} cm^2/s)	S (cm^3STP/ cm^3 cmHg)	P (barrer)
A	4.4	0.0110	0.048
B	4.7	0.0149	0.070

Fick's law, the flux of a penetrant through a membrane is proportional to the local concentration gradient:

$$J = D\nabla C \qquad (6)$$

If D and S are assumed to be independent of concentration, the steady-state permeation rate (J) through a membrane can be described as[15]

$$J = DS\frac{\Delta p}{l} = P\frac{\Delta p}{l} \qquad (7)$$

Δp being the difference of penetrant pressure across the membrane.

In the present work, we used two different permeability coefficients, depending on the units in which the concentration gradient of the penetrant is expressed. Since we introduced pure solvents inside the gravimetric cell, we assumed that the pressure of the penetrant inside the cell corresponds to the vapor pressure of the solvent at the corresponding temperature (P_v). So, we can rewrite the above relation as

$$P = \frac{Q}{A}\frac{l}{(P_v - P_{ext})} \qquad (8)$$

where Q is the slope of the steady-state part of the permeation plot; A, the exposed area of the film (2.54 cm^2 in our case); P_{ext}, the external pressure of the solvent (assumed to be zero for the organic solvents); and P, the permeability coefficient in barrers (10^{-10} cm^3 STP cm/cm^2 s cm Hg). When measuring water permeability, P_{ext} can be calculated from the relative humidity of the surrounding ambient (measured using a thermohygrometer) and the water vapor pressure at 30°C.

Vapors of substances that are liquids at normal pressures and temperatures do not obey Henry's law, and, consequently, the permeability coefficient is not proportional to the pressure differential across the membrane.[16] Under this point of view, it is possible to interpret that the driving force of the process is better characterized by the solvent activity, which is equal to 1 inside the cell. With this in mind, we can write

$$\text{VTR} = \frac{Q}{A}\frac{l}{(1 - a_{ext})} \qquad (9)$$

where a_{ext} is the penetrant activity outside the cell (assumed to be zero for the organics and equal to the relative humidity in the case of water) and VTR is the vapor transmission rate coefficient in (g cm/cm^2 s). The basic features of the two coefficients defined by eqs. (8) and (9) are that the former is a coefficient normalized to the vapor pressure of the penetrant, which can vary as much as one order of magnitude from one solvent to another, and the latter is proportional to the actual flux of the penetrant passing through the membrane.

To calculate diffusion coefficients, the total amount of a diffusing substance which has passed through a membrane in time $t(Q_t)$ can be expressed as[14]

$$Q_t = \frac{DC_1}{l}\left(t - \frac{l^2}{6D}\right) \qquad (10)$$

provided that time is long enough (i.e., the steady state has been reached). In this equation, C_1 is the concentration of the penetrant in the inner surface of the membrane, being zero in the outer surface. The intercept of this line with the time axis is called the time lag, given by

$$L = \frac{l^2}{6D} \qquad (11)$$

from which D can be calculated if, as previously mentioned, it is supposed to be independent of the penetrant concentration across the membrane. In general, this is not the case when working with organics in polymers, but the lack in $D(c)$ vs. concentration data for PHB has led us to use the above equation as an approximated way to calculate diffusion coefficients. However, in some cases, where the extrapolation was not accurate enough or the system showed anomalous permeation plots, the obtention of time lags in a straightforward manner was prevented. Consequently, the calculation of D must be viewed with caution. It has been shown[17] that, for many systems, the following inequality holds for a wide range of functional dependencies of $D(c)$ on concentration:

$$\frac{1}{6} \leq \frac{LD}{l^2} \leq \frac{1}{2} \qquad (12)$$

Thus, an estimate of D (intended as an average diffusion coefficient across the membrane) may be too small by a factor of 3. However, if comparisons are made between diffusion coefficients ob-
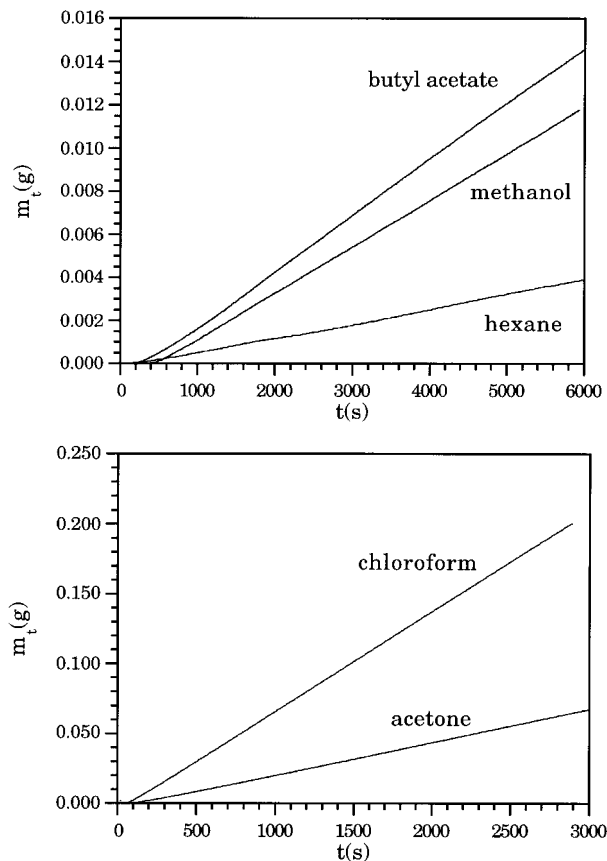
Figure 3 (a) Permeation plots of butyl acetate, hexane, and methanol through PHB. (b) Permeation plots of chloroform and acetone through PHB.

tained in similar conditions for a given system, this order of accuracy may be sufficient.[18] Guo et al.,[13] after comparing data from both sorption and permeation experiments, proposed that the diffusion coefficients obtained in this manner are an average heavily weighted in the lower concentration side of the membrane.

Some typical permeation plots are illustrated in Figure 3(a) and (b). The permeation rate (i.e., the slope of the weight loss vs. time plot), initially zero, gradually increases until a steady state is reached, which is characterized by a straight line.

The relative variation of the permeability of a set of solvents can be better outlined graphically. In Figure 4(a), the results of the vapor transmission rate [see eq. (9)] are presented. Among the different penetrants studied, we selected nine, which, apart from being representative of different functional groups, can be classified into three categories, in relative terms of permeation characteristics: (1) high vapor transmission rate solvents—acetone and chloroform, (2) medium va-

por transmission rate solvents—butyl acetate, toluene, methanol, and carbon tetrachloride, and (3) low vapor transmission rate solvents—water, isopropyl ether, and n-hexane. The differences in permeability among them are of about 1 order of magnitude. It is interesting to note that the vapor transmission rate values here presented are directly proportional to the actual flux of the penetrant across the membrane, since the exposed area, thickness, and activity of the vapor are always the same—see eq. (9)—except for the case of water.

With the aim of clarifying to what extent the vapor pressure influences the transport process, we also calculated the permeability coefficient in barrers [eq. (8)]. The permeability coefficient has the feature of including the solvent vapor pressure (cmHg), so that the mass flux rate becomes normalized not only to the sampling area and thickness, but also to the pressure exerted by the penetrant. Results are graphically shown in Figure 4(b), evidencing a more gradual variation in the permeability of the solvents of interest. This fact demonstrates that the differences in the va-
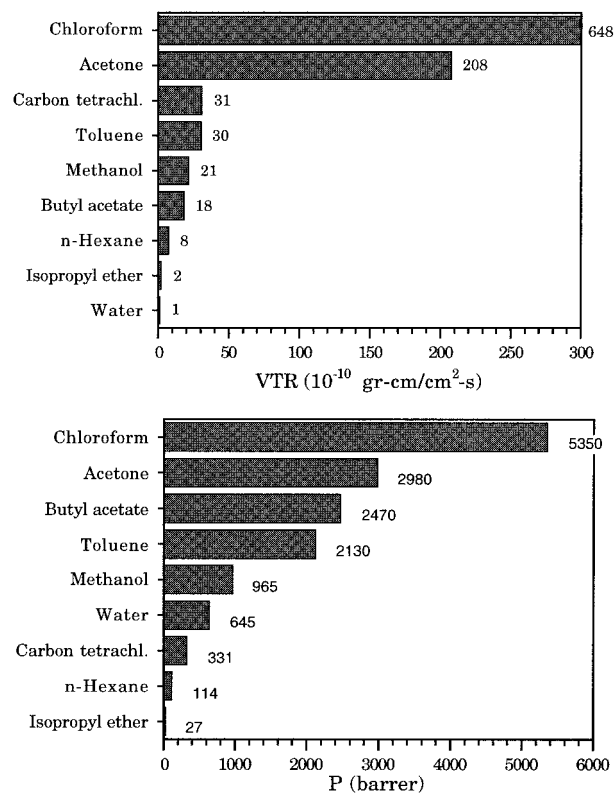

Figure 4 (a) Vapor transmission rates of various vapors through PHB. (b) Permeabilities of various vapors through PHB.

Table III   Vapor Permeation Experiments

Solvent	D $(10^{-9}$ cm^2/s$)$	VTR $(10^{-10}$ g cm/cm^2 s$)$	P (barrer)
Chloroform	10	648	5070
Acetone	5.0	208	2830
Butyl acetate	1.8	18.4	2340
Toluene	2.2	30.4	2020
Methanol	0.74	21.4	914
Water[a]	[b]	1.34	529
Carbon tetrachloride	0.98	30.6	314
n-Hexane	[b]	7.52	108
Isopropyl ether	[b]	2.09	25.2

[a] Relative humidity difference across the membrane: 100–33%

[b] The extrapolation of the steady-state permeation plot to obtain time lags and diffusion coefficients in these cases was not enough accurate to give a reproducible value.

por transmission rate values of Figure 4(a) are mainly due to differences in the vapor pressure of the penetrants. The permeabilities and diffusivities obtained for these vapors are shown in Table III.

To better understand the implications of using the permeability coefficient instead of the vapor transmission rate, we will consider an example: Figure 4(a) shows that toluene and carbon tetrachloride have the same vapor transmission rate. On the other hand, from Figure 4(b), we learn that the permeability coefficient ratio for toluene and carbon tetrachloride is approximately 6 : 1. In other words, the permeability coefficient representation reveals that toluene is more "effective" as a penetrant than is carbon tetrachloride, since more toluene passes through the membrane for each cmHg of pressure applied. This effect is even more pronounced for butyl acetate, which shows the greatest relative change from one figure to the other, revealing that, although having a low vapor pressure at 30°C, a great flux rate per unit of applied pressure is achieved.

Additional evidence of the differences between data in the units of the permeability coefficient and vapor transmission rate can be seen in Figure 5(a) and (b). In Figure 5(a), vapor transmission rate data from a series of penetrants composing a family of chlorinated solvents and other chlorine-free solvents are shown. The general trend of a decreasing vapor transmission rate when increasing the molar volume is observed. On the other hand, Figure 5(b) shows that using permeability its dependence on the molar volume becomes less evident if noninexistent; moreover, the chlorinated solvents occupy the upper part of the graph with the exception of carbon tetrachloride.

It is well known that some chlorinated solvents can dissolve PHB (CH_2Cl_2, $CHCl_3$, $C_2H_2Cl_4$). This means that some kind of molecular interaction exists between PHB and this type of species. 1,4-Dichlorobutane and carbon tetrachloride do not dissolve PHB, but while the former has a quite high permeability coefficient (which shows that it is capable of having some degree of interaction with the polymer despite not dissolving it), the later has a very low one. This behavior is somewhat expected since CCl_4, not having hydrogen in the vicinity of the C—Cl bonds, and being a fully apolar molecule, does not interact with the polyester chains.

Variations in the PHB transport properties can be related to other characteristic parameters of the penetrants. One of them is the solubility parameter. Figure 6 shows that the vapor transmission rate values of a series of analog ketones fall in a straight line when plotted against the solubility parameter. However, cyclohexanone, having a different, bulky structure, drops out of this line. This trend can also be found when comparing other solvents. In Figure 7, a different relationship seems to correlate the vapor transmission rate and solubility parameters when solvents of different chemical structure are included together in a similar plot (the data of water and methanol have not been included there for the sake of clarity). The vapor transmission rate (in a logarithmic scale) tends to increase when the penetrant solubility parameter approaches the poly(hydroxybutyrate) value[6] of 20.6 J$^{1/2}$/cm$^{3/2}$.

Liquid Permeation Experiments

When working with liquids in contact with the membrane, we use the liquid transmission rate
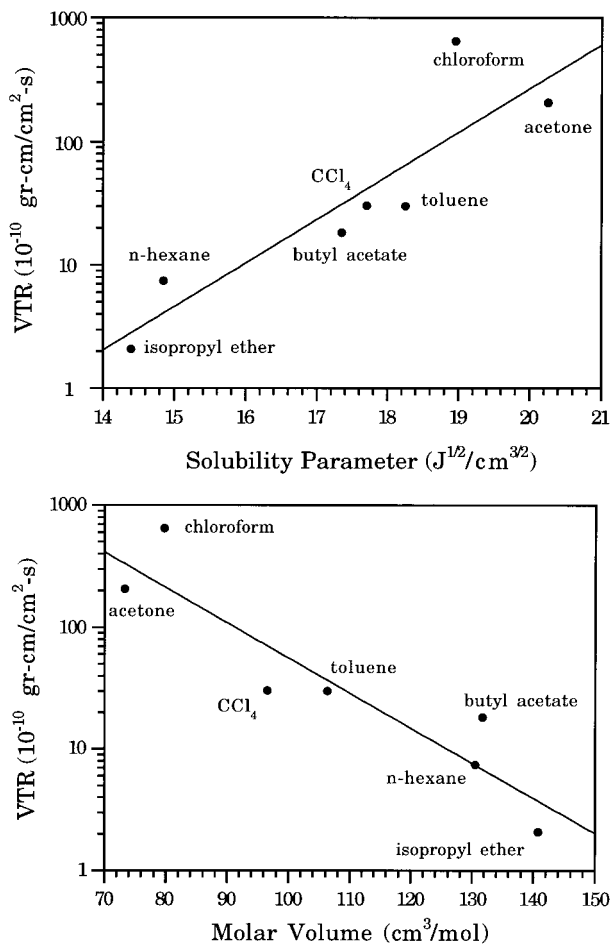
Figure 5 (a) Vapor transmission rates for both chlorinated and nonchlorinated solvents: (●) chlorinated solvents; from left to right: dichlorometane, 1,2-dichloroethane, chloroform, carbon tetrachloride, 1,1,2,2,tetrachloroethane, 1,4-dichlorobutane (1,4 DCB). (○) Nonchlorinated solvents; from left to right: acetone, methyl ethyl ketone, cyclohexanone, 3-pentanone, toluene, methyl isobutyl ketone, butyl acetate, isopropyl ether. Data obtained at 23°C. (b) Permeability data for both chlorinated and nonchlorinated solvents. Same symbols than in Figure 5(a). Data obtained at 23°C.

(LTR) coefficient, which is analogous to the VTR coefficient described for vapors in eq. (9). The results are summarized in Table IV. It also contains the ratio between the liquid and vapor transmission rates for each penetrant studied. The liquid transmission rate is in average three times higher than that of the vapors in most of organic substances, although for methanol, isopropyl ether, and carbon tetrachloride, it is almost equal. The quotient for water is 31, which is exceedingly higher than expected. To explain this striking phenomenon, we calculated the work of adhesion
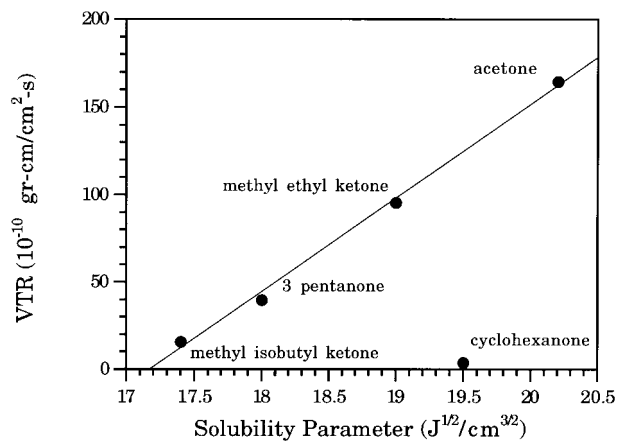

Figure 6 Correlation of vapor transmission rate data vs. solubility parameter for a series of homologous ketones in PHB. Data obtained at 23°C.
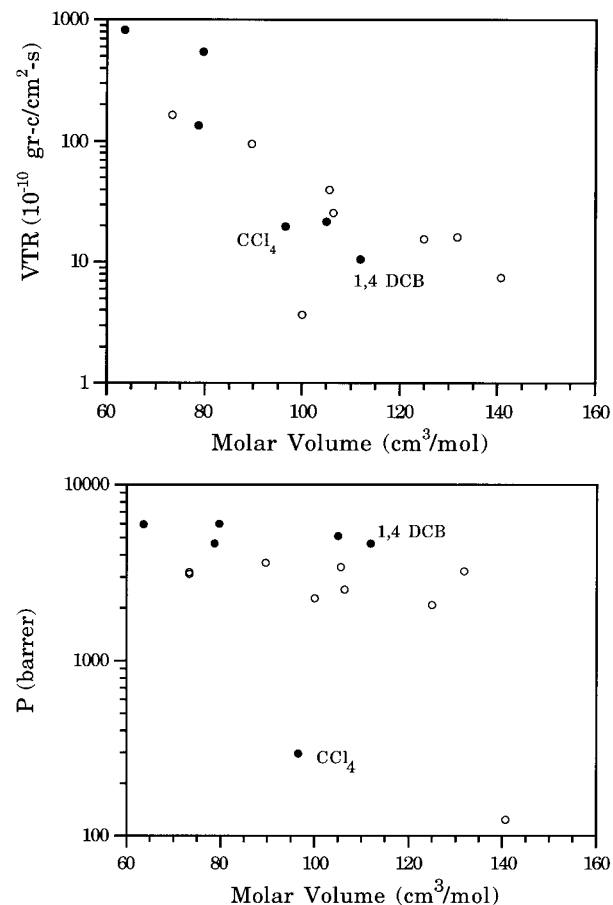

Figure 7 Correlation of vapor transmission rate data vs. solubility parameter for organic vapors through PHB. Data obtained at 30°C.

Table IV Liquid Permeation Experiments

Solvent	D (10^{-9} cm^2/s)	LTR (10^{-10} g cm/cm^2 s)	LTR/VTR
Chloroform	11.8	3310	5.1
Acetone	9.4	490	2.4
Butyl acetate	2.7	65.5	3.6
Toluene	3.2	105	3.5
Methanol	a	31.6	1.5
Water[b]	c	42.1	31
Carbon tetrachloride	a	34.6	1.1
n-hexane	a	28.7	4.4
Isopropyl ether	a	2.78	1.3

 a Systems showing anomalous permeation plots.
 b Relative humidity difference across the membrane: 100−33%.
 c The extrapolation of the steady-state permeation plot to obtain time lags and diffusion coefficients in these cases was not enough accurate to give a reproducible value.

between water and PHB using the Young's equation[19]:

$$W_{adh}(\text{polymer/water}) = \gamma_w(1 + \cos \alpha)$$

γ_w being the surface tension of water (72.75 mN/m), and α, the contact angle between water and PHB. The value of α, estimated using approximated methods,[20] is about 45°. Consequently,

$$W_{adh}(\text{PHB/water}) \approx 124 \text{ mN/m}$$

The work of cohesion for water is

$$W_{coh}(\text{water}) = 2 \cdot \gamma_w = 146 \text{ mN/m}$$

Therefore, the work of adhesion at the water/PHB interface is almost as high as is the work of cohesion of the water itself, showing that a good contact is achieved between both phases. Furthermore, the value of 124 mN/m is very high compared to those of the organic compounds studied, having works of adhesion which are always under 60 mN/m (in the best case, supposing a contact angle of 0° for the system toluene/PHB, W_{adh} = 57 mN/m). So, the high interfacial energies that take place in the case of water could be the source of the additional driving force that is responsible for the high LTR/VTR of water.

Permeation Anomalies

During our experiments with PHB and a wide range of different solvents, we found some cases in which the liquid permeation curves did not follow the ex-

pected behavior. In these conditions, after a few seconds in which no weight loss takes place, a sharp increase in the permeation rate is observed until it passes through a maximum, decreases, and eventually approaches a steady-state level. One of these situations is reproduced in Figure 8, where the vapor permeation plot is also shown for comparison. Anomalous permeation curves of this type were found for carbon tetrachloride, *n*-hexane, isopropyl ether, and methanol.

This kind of behavior was observed by many other workers in the past.[21–23] Some explanations have been proposed. Meares[21] suggested that for a good solvent or swelling agent an equilibrium between the liquid and the ingoing face of the polymer is instantaneously established. So, the
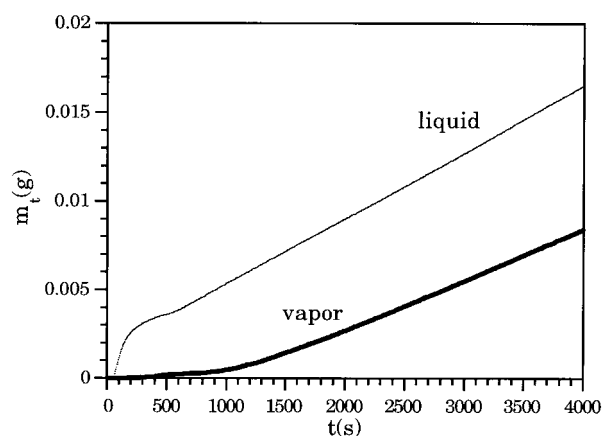

Figure 8 Permeability plots for carbon tetrachloride at 30°C illustrating the difference between vapor and liquid ("anomalous") experiments.

Table V Water Vapor and CO_2 Permeabilities of Some Common Polymers at 25°C

Material	Carbon Dioxide,[24] P (barrer)	Water Vapor,[18] P (barrer)
PVDC	0.02	3−10[a]
PVC	0.15	280[b]
Nylon 6,6	0.17	680[c]
PET	0.3	130
PP	2.9	51
Cellulose acetate	6.0[d]	5500
LDPE	12.6	90
PHB[e]	0.048	529

[a] Dependent on grade.
[b] Ref. 25.
[c] At 95% HR.
[d] At 35°C, Ref. 26.
[e] At 30°C, this work.

molecular layers at this face would swell and expand, straining the underlying polymer, and making it less dense and more permeable. For the case of poor swelling agents, Petropoulos and Roussis,[23] suggested that the initial transport could be attributed to single penetrant molecules. As the process goes on, the tendency of the polymer−penetrant system to approach the thermodynamically most favorable configuration of minimum energy could lead penetrant molecules to cluster if possible. This would result in reduced mobility of the moving especies, and if this process goes far enough, a tendency to a decrease of the permeability could be observed. This explanation could apply qualitatively in the case of PHB.

Finally, a third hypothesis could be the following: Given that the species which led to anomalous behaviors do not have strong interaction with the polymer, it is likely that the molecular relaxations of the latter to accommodate the penetrant have been quite slow. In this way, the amorphous parts constrained by the presence of the crystallites would have a high permeability due to structural irregularities. That would lead to a reduced free volume after relaxing, as well as to a reduction in the permeability. More interacting penetrants would be capable of relaxing the polymer chains almost instantaneously when entering the structure showing the "normal" behavior, while the noninteracting penetrants would need more time to do this, showing the anomalous plots.

The fact that the anomalies occurred only in liquid experiments could be explained as follows: As we see from Figure 8, by the time the first weight loss was detected in the vapor experiment (about 500 s), the anomalous behavior disappeared in the liquid experiment. It can be interpreted that the first few molecules coming from the vapor phase that enter the membrane are capable of conditioning the polymer, before a substantial amount of matter has permeated. With liquid, due to its higher concentration and perhaps to some kind of interfacial effects, a certain amount of permeation is achieved even before the conditioning process has ended, giving rise to the anomalies.

CONCLUSIONS

Water and CO_2 permeability data[18,24–26] of some polymers, comprising those to which PHB has been often compared in terms of barrier properties (PVC, PP, PET)[10−12] are shown in Table V. There are few data about pure organic solvent perme-

Table VI Vapor Transmission Rates (10^{-10} g cm/cm² s) of Some Organic Solvent–Polymer Systems at 20°C

Material	Chloroform[28]	Acetone[28]	Methanol[28]	Carbon Tetrachloride	Toluene
PVC	33	30	0.006		
PA	3.2	0.26	52		
PET	10	0.39	0.030	0.034[16]	
LDPE	354	3.0	0.53	277[a]	231[a]
Cellophane	1776	X	252		
PHB[b]	648	208	21.4	30.6	30.4

[a] X: dissolved.
[a] At 40°C, Ref. 29.
[b] At 30°C, this work.

Table VII   Water Vapor and CO_2 Permeabilities of Some Biodegradable Polymers[31]

CO_2, P (barrer)[a]		Water Vapor, P (barrer)	
Pectin	64.5	Starch	430,000[b]
Wheat gluten	111	Wheat gluten and carnauba wax	11,800[c]
Chitosan	24	Wheat gluten and beeswax bilayer	70[c]

[a] 25°C.
[b] 38°C, 30–100% RH.
[c] 30°C, 0–100% RH.

ation in the literature, as well as in great diversity of units, which makes it difficult to establish comparisons[27]; however, some selected data[16,28,29] are presented in Table VI. Finally, PHB is compared in Table VII with some biodegradable polymers.

From all the above comparisons, we can conclude that PHB can be considered a high barrier polymer for CO_2, having a permeability close to poly(vinylidene chloride). The water transmission rate is close to nylon 66, having also similar CO_2 permeability; so we can say that PHB is a medium barrier polymer for water.

PHB has a low barrier character for organic solvents, as we can see in Table VI. Following the general trend of permeability and diffusivity being higher when the penetrant and the polymer are similar,[30] PHB showed the lowest barrier properties with moderately polar solvents (acetone, chloroform) and the highest with apolar ones (hexane, CCl_4).

Finally, when compared to other biodegradable polymers, PHB shows a very good balance of barrier properties as regards to water and CO_2. Besides, it has the great advantage of its moisture insensitivity and low hydrophilic character, a common drawback of this kind of polymers.[31] For all these reasons, PHB seems to be one of the most promising biopolymers for designing a future ecological packaging.

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