

Gas Transport in Surface-Modified Low-Density Polyethylene Films with Acrylic Acid as a Grafting Agent

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ABSTRACT: The modification of polyethylene by the grafting of poly(acrylic acid) onto the surface of one of the faces of low-density polyethylene films with UV radiation is reported. The transport of oxygen, nitrogen, carbon monoxide, carbon dioxide, methane, ethane, ethylene, propane, and argon across surface-modified films containing 3.7% poly(acrylic acid) has been investigated at several temperatures. The layer of poly(acrylic acid) grafted onto the surface of one of the faces of the films reduces the permeability coefficient of the gases by a factor of about 1/6. The sharp drop in the gas permeability as a result of the poly(acrylic acid) layer may arise either from the formation of ordered structures of the grafted chains or from the development of highly crosslinked structures. The values of the polymer–gas enthalpic interaction parameter for the modified film are higher than those for the unmodified one. © 2006 Wiley Periodicals, Inc. *J Polym Sci Part B: Polym Phys* 44: 2828–2840, 2006

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INTRODUCTION

For many applications, changes and improvements in some of the polymeric surface properties of materials are important issues.¹ Among the materials for which the need of surface modifications is felt, polyolefins stand out.^{2–4} Modified polyolefin surfaces may display a number of new properties, such as adhesion improvements,^{5,6} compatibilization,^{7–9} wettability,⁸ and functionalization.^{9,10} Surface chemical modification can be performed through the surface grafting, onto polymer films, of suitable monomers containing functional groups that can be used for further reactions. In this way, functional groups such as amine, imine, hydroxyl, carboxylic acid, sulfate,

and epoxy groups can be incorporated onto the surface of a broad range of conventional polymeric substrates, most of which have a nonpolar, less reactive surface.¹¹ Surface grafting may proceed by free-radical mechanisms generated by oxidants such as Ce^{+4} ions¹² and peroxide initiators.¹³ High-energy radiation, γ or electron-beam radiation, and low-energy radiation, such as UV light, are frequently used to create radical mechanisms that promote polymer grafting reactions.^{2,14–16}

The chemical and/or physical modification of film surfaces may affect their barrier properties. As is well known, gas transport under a unidirectional, negative chemical potential driving force perpendicular to the film surface involves the dissolution of the gas in the film, the diffusion of the gas across the film, and the desorption of the gas at the other side of the film. These steps depend on the physical state of the film: glassy, rubbery and amorphous, or semicrystalline. At first glance, gas

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permeation through semicrystalline polymers seems to be a rather complex process because crystalline entities act as impermeable barriers, forcing the penetrants to travel longer paths in the crystalline/amorphous interface than in the amorphous region, thus reducing the diffusion coefficient. Moreover, gases are insoluble in the crystalline phase. Despite this, gas transport through semicrystalline films is a simple process in the sense that if phase transitions are absent in the range of temperatures assayed, the variation of the gas permeability coefficients with the temperature obeys Arrhenius behavior. Earlier studies^{17–19} have shown that both annealing and drawing processes affect the permeability characteristics of linear low-density polyethylene (LLDPE). For example, annealing causes a significant enhancement of the permeability coefficient.¹⁷

Although a variety of work on gas transport through modified polymeric materials has been reported,^{20–26} the studies of gas permeation across surface-grafted low-density polyethylene (LDPE) films are relatively scarce. Huang and Kanitz²⁷ reported the permeation of gases through polyethylene–styrene graft copolymers prepared by the mutual γ radiation of LDPE films in styrene–methylene solutions over a wide grafting percentage window. They found that the permeability coefficient decreases with increasing grafting to minimum values at 20–30% and increases again above 30% grafting. The decrease in the permeation was attributed to the decrease in the free volume caused by the glassy polystyrene chains, whereas the increase in the gas permeation above 30% presumably arises from the disruption of crystallites of LDPE.

This work reports the surface grafting of poly(acrylic acid) onto one of the faces of LDPE films with UV radiation with the aim of investigating the effect of the grafted layer on gas transport. In this case, the complexity of the permeation across polyethylene is enhanced by the glassy poly(acrylic acid) layer covering the surface of the films, which acts as a first barrier in the transport process. It is important to study how the hydrophilic and glassy character of poly(acrylic acid) may affect the diffusion and solubility coefficients of different gases through the surface-grafted films. In this context, the transport of oxygen, nitrogen, carbon dioxide, argon, carbon monoxide, methane, ethane, ethylene, and propane through surface-grafted LDPE films is investigated. To obtain deeper insight into how the poly(acrylic acid) surface layer influences the barrier properties, the permeation

characteristics of the LDPE films prior grafting have also been studied.

EXPERIMENTAL

Materials and Reagents

Acrylic acid (BASF), acetone (Cicarelli), ethanol (Porta), NaOH (Cicarelli), and benzophenone (Fluka AG) were commercially acquired and used as received, without further purification.

LDPE films 47 μm thick were kindly provided by Vitopel (Argentina). The melting behavior of LDPE was determined by differential scanning calorimetry at a heating rate of 20 $^{\circ}\text{C}/\text{min}$. The crystallinity degree, calculated from the melting endotherm (assuming that 960 cal/mol of CH_2 was the value of the melting enthalpy of 100% crystalline polyethylene),²⁸ was 39%.

Graft Copolymerization Procedure and Characterization

A dry film of polyethylene, previously washed with distilled water, was placed in a glass Petri dish. To 0.5 mL of a 0.2 M solution of benzophenone in acrylic acid, 0.5 mL of distilled water was added, and the resulting solution was poured into the dish containing the film. Nitrogen was continuously bubbled into the solution to remove oxygen, and the dish containing the reactants was irradiated with UV light (medium-pressure UV lamp, Engenhard–Hanovia) at room temperature under a nitrogen atmosphere. The grafted sample was extensively washed before analysis with a very dilute NaOH solution (pH 8) to remove the rest of both the unreacted monomer and the homopolymer formed and to take out the rest of the initiator.

The grafting percentage was quantified by both gravimetric measurements and volumetric titration of the $-\text{COOH}$ groups grafted onto the surface of the films with a NaOH solution. The grafting percentage is given by

$$\text{Grafting (\%)} = 100 \times (\text{Weight of grafted LDPE} - \text{Weight of LDPE}) / (\text{Weight of LDPE}) \quad (1)$$

Infrared (IR) Spectroscopy

Fourier transform infrared (FTIR) spectra of the grafted film (10 scans and 32 resolutions) were obtained with a Nicolet 5 SXC spectrometer.

Surface Analysis by Atomic Force Microscopy (AFM)

AFM measurements were performed at room temperature in air with a commercial optical lever microscope (Multimode Nanoscope III, Digital Instruments). The tapping-mode height and phase images were recorded with etched silicon probes with a force constant of 20–100 N/m and a resonance frequency of 195 kHz. The free amplitude and set-point amplitude were modified according to the experimental requirements. The scanning rate was 1 Hz.

X-Ray Diffraction (XRD)

XRD measurements were conducted on modified and unmodified polyethylene. The diffractograms were obtained with Ni-filtered Cu K α radiation (wavelength = 1.5405 Å at 40 kV and 25 mA) generated by a Philips diffractometer.

Gas Permeation Measurements

Gas transport measurements were performed in an experimental device made up of two compartments separated by the film. A high vacuum was made in the two compartments, and then gas at a given pressure was suddenly introduced into one of the two compartments, called hereafter the upstream chamber, provided with a Gometrics pressure sensor (0–10 bar). The gas flowing from the upstream chamber to the other compartment, or downstream chamber, was monitored as a function of time with an MKS pressure sensor (10^{-4} –1 mmHg) via a personal computer. The permeation equipment was immersed in a water thermostat at the temperature of interest.

The permeation coefficient (P) was obtained with the following expression:

$$P = \frac{273}{76} \left[\frac{V_d L}{AT p_u} \right] \lim_{t \rightarrow \infty} \frac{dp_d(t)}{dt} \quad (2)$$

where V_d , A , l , and T represent the volume of the downstream chamber, area of the barrier, barrier thickness, and temperature, respectively, whereas p_d and p_u are the pressures of the downstream and upstream chambers, respectively. P is usually given in barrers [1 barrer = $10^{-10} \times \text{cm}^3(\text{STP})/(\text{cm}^2 \text{ s cmHg})$]. Under steady-state conditions, the amount of gas flowing per unit of area through the membrane up to time t

[$Q(t)$] is given by^{29,30}

$$Q(t) = \frac{DC_u}{l} \left(t - \frac{l^2}{6D} \right) \quad (3)$$

where D is the diffusion coefficient and C_u is the concentration of the gas at the upstream chamber. By calling θ the time lag at which the plot of p_d versus t intercepts the abscissa axis, D can be obtained from the following expression:³¹

$$D = \frac{l^2}{6\theta} \quad (4)$$

The apparent solubility coefficient (S) can be calculated from P and D with the following equation:

$$S = P/D \quad (5)$$

Transport parameters D and S are usually given in cm^2/s and $\text{cm}^3(\text{STP})/(\text{cm}^3 \text{ cmHg})$ units, respectively.

Sorption Measurements

Sorption experiments of ethylene in a small piece of a film of poly(acrylic acid) were carried out with a Cahn D-200 balance. The balance registered automatically, at a given pressure, the gas sorption as a function of time with a precision of 0.1 μg via a personal computer. D can be obtained from the following equation:

$$\ln \left(1 - \frac{M_t}{M_\infty} \right) = \ln \left(\frac{8}{\pi^2} \right) - \frac{\pi^2 D}{l^2} t \quad (6)$$

where M_t and M_∞ are the masses of gas absorbed in mass m of poly(acrylic acid) at time t and infinite time, respectively. The sorption coefficient can directly be obtained from M_∞ and m , whereas D is determined from plots of $\ln(1 - M_t/M_\infty)$ versus t , as eq 6 suggests.

RESULTS AND DISCUSSION

Chemical Modification

Previous studies of the grafting reaction conditions have shown that the use of water and benzophenone as the solvent and initiator, respectively, improves the grafting efficiency of acrylic

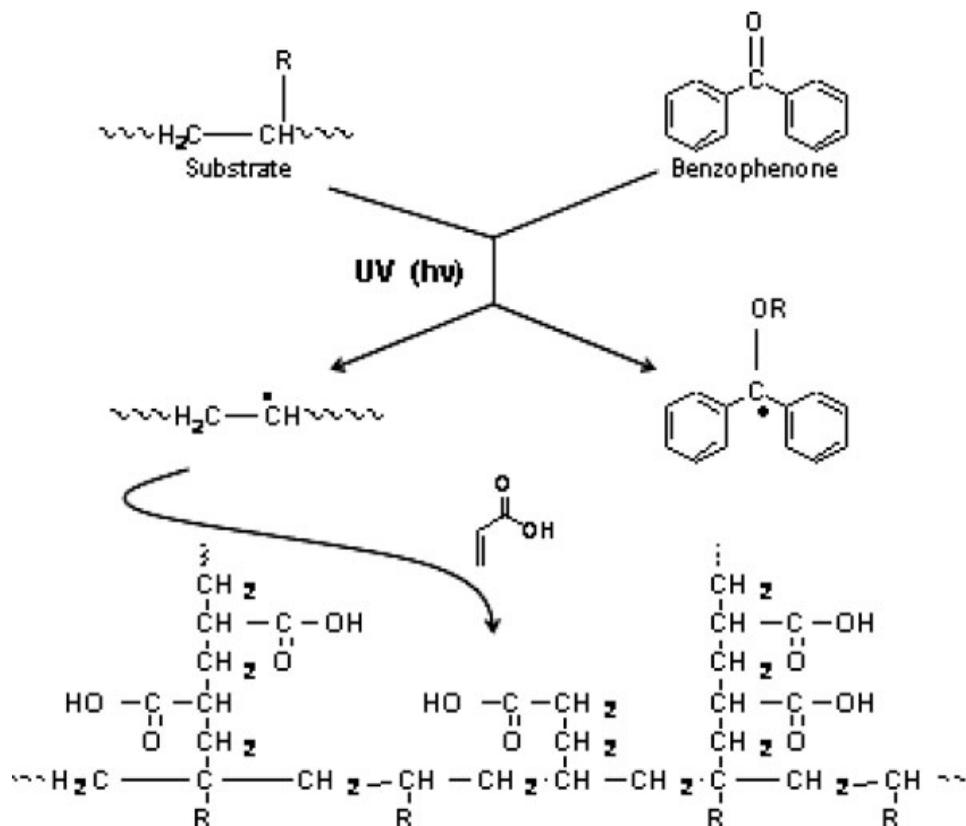


Figure 1. Grafting mechanism of acrylic acid onto LDPE (R = H).

acid onto LDPE films.³² The grafting mechanisms are presented in Figure 1. For surface-modification applications, thick grafting layers are unnecessary and even undesirable because they may change the physical properties of the bulk polyethylene. The presence of water in the reaction medium promotes the formation of surface-grafted thin layers because it prevents the diffusion of the monomer inside the polymer film. Moreover, the grafting agent and the grafted chains are soluble in water, and this fact facilitates radical reaction propagation outside the polymer surface. In addition, water is inert to the triplet excited state of the benzophenone photoinitiator, so the grafting reaction is not inhibited.³³ The rest of the homopolymer that was formed was removed by exhaustive washing of the grafted films with a very slightly basic solution (pH 8) and then with distilled water (pH 6). The IR spectra of the grafted films before the washing process showed a large signal from C=C groups at 1613 and 810 cm^{-1} , indicative of the presence of the unreacted monomer; this signal disappeared after the rinsing of the grafted films.

The modified films were characterized with FTIR spectroscopy. Representative IR spectra at different irradiation times are shown in Figure 2. Typically, an intense $\text{C}=\text{O}$ absorption (1718 cm^{-1}) characteristic of poly(acrylic acid) could be seen in the spectra. Other typical bands of polyethylene were observed at 1472 and 1462 cm^{-1} (CH_2 and CH_3 bending) and at 719 and 729 cm^{-1} (CH_2 rocking). The evolution of the 1718 cm^{-1} ($\text{C}=\text{O}$)/719 cm^{-1} (CH_2) intensity ratio with the reaction time is shown in the second column of Table 1, whereas the grafting percentage obtained by the gravimetric method is given in the third column of the table. In the fourth column of the table, the grafting percentages obtained at short times by volumetric titration agree satisfactorily with those determined by gravimetry.³² Grafted poly(acrylic acid) chains are not detected by transmission FTIR at grafting times lower than 3 min, as the spectra of Figure 3 suggest. At times greater than 3 min, the grafting percentage is a linear function of time. In general, the values of the grafting percentage obtained by the two methods agree

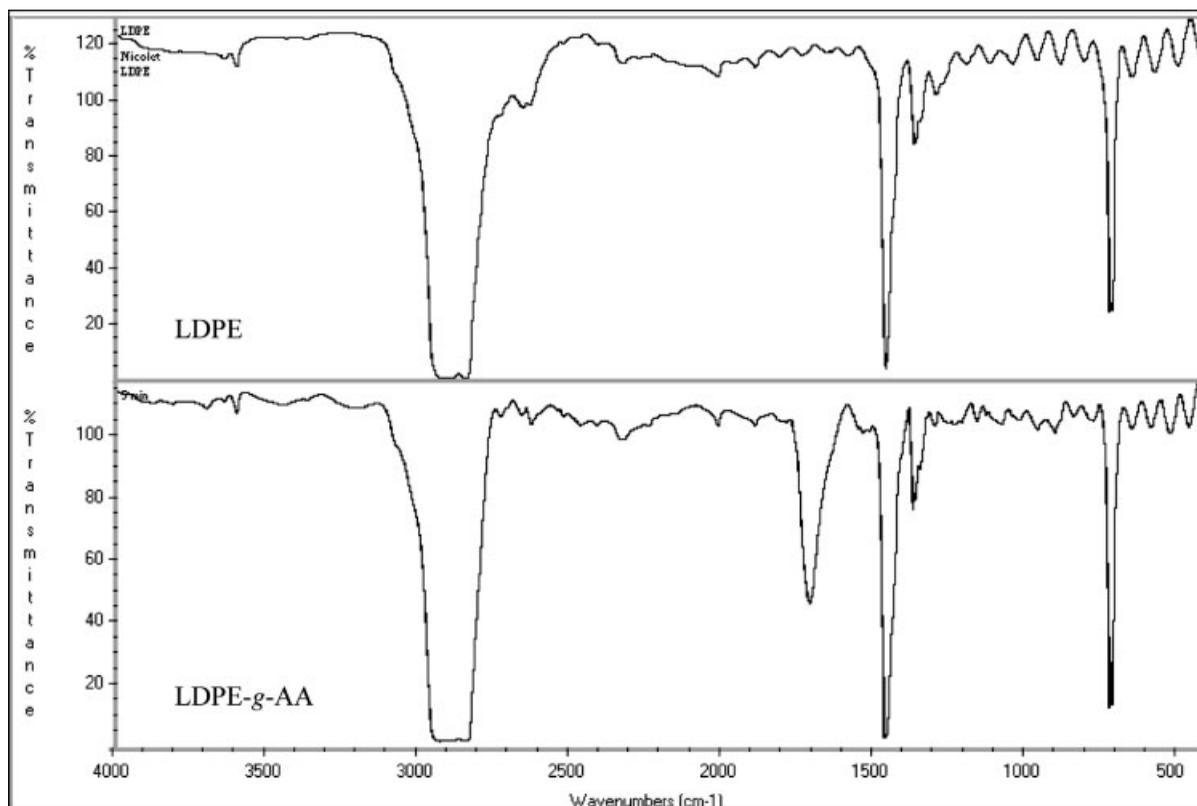


Figure 2. Representative FTIR spectra for LDPE and LDPE with a grafting percentage of 3.7%.

pretty well in a wide range, as the results of Figure 4 show.

Gas Permeation

The experiments were carried out with the modified and unmodified film surfaces facing the upstream and downstream chambers, respectively. The fourth and fifth columns of Table 1 show the variation of the P and D values of pro-

pane through LDPE films as a function of the grafting time, respectively. For grafting times shorter than 3 min, the transport properties of the surface-modified films are similar to those of LDPE. However, P experiences a sharp drop as the grafting time increases. The values of P and D decrease from 7.54 to 0.99 barrers and from 3.1×10^{-8} to 1.3×10^{-8} cm²/s, respectively, when the grafting time increases from 2 to 5 min.

Table 1. Variation of the Intensity (I) of the 1718-cm⁻¹ IR Band, the Transport Properties of Propane at 30 °C, and the Grafting Percentage of Poly(acrylic acid) onto LDPE as a Function of the Grafting Time

Time (min)	I (1718 cm ⁻¹)/ I (719 cm ⁻¹)	Grafting (%) ^a	-COOH/cm ² (μequiv) ^b	P (barrer)	$10^7 \times D$ (cm ² /s)
0	0	—	—	7.35	0.31
2	0	—	—	7.54	0.31
3	0.036	—	—	6.85	0.25
4	0.218	1.1	0.12	3.13	0.16
5	0.358	3.7	3.20	0.99	0.13

^a As determined by gravimetric measurements.

^b As determined by volumetric titration.

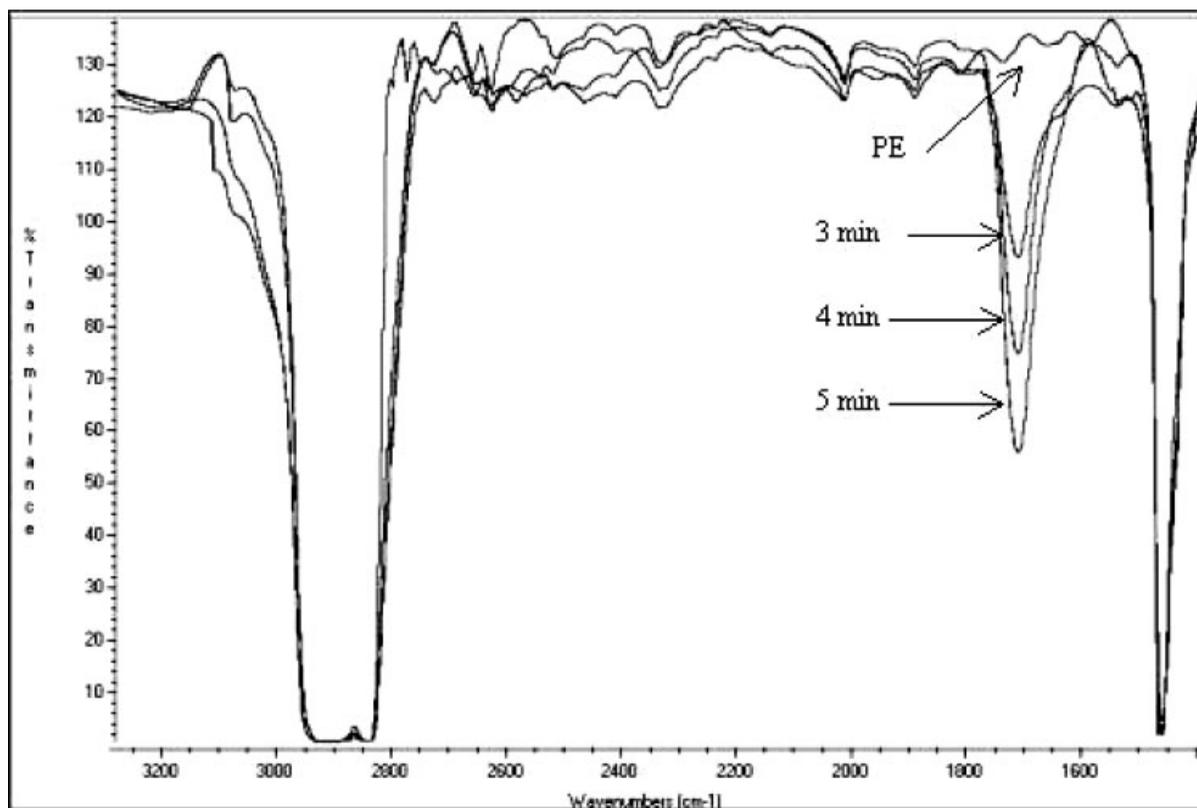


Figure 3. FTIR spectra showing representative bands of LDPE and modified (grafting percentage = 3.7%) LDPE films at different reaction times (PE = polyethylene).

Let us consider in detail gas transport through modified LDPE films containing a grafting percentage of poly(acrylic acid) of 3.7%. An illustrative isotherm showing the time dependence of the pressure of propane in the downstream chamber at 30 °C is shown in Figure 5. Despite the complexity of the morphology of the grafted films, the evolution of the pressure in the downstream chamber with time is described by the expression resulting from the integration of Fick's second law,³⁰ represented by a continuous line in the figure. The curve shows a transitory permeation process at short times followed by a linear dependence of the pressure on time that reflects steady-state conditions. The intersection of the straight line with the abscissa axis gives time lag θ . From the slope of the straight line of $p_d(t)$ versus t and θ , the values of P and D are obtained by means of eqs 2 and 4, respectively. In turn, S is calculated from the values of P and D with eq 5.

Values at 30 °C and 1 bar of P for oxygen, nitrogen, carbon dioxide, argon, carbon monoxide, methane, ethane, ethylene, and propane

through the modified films are shown in the fifth column of Table 2. For comparison, the values of P of the gases across the unmodified films are given in the second column of the table. The values of P undergo a sharp drop, the ratio $\beta = P(\text{unmodified film})/P(\text{modified film})$ reaching a maximum for propane ($\beta = 7.4$) and a minimum for carbon dioxide ($\beta = 5.0$). The average value of β for the investigated gases is 6.5 ± 0.7 .

The pertinent values of D for the modified and unmodified LDPE films are shown in the third and sixth columns of Table 2, respectively. The fall experienced by D due to the surface modification is smaller than that of P . Thus, the ratio $\gamma = D(\text{unmodified})/D(\text{modified})$ reaches a minimum of 1.6 for carbon monoxide and a maximum of 2.9 for carbon dioxide, the average value of γ being 2.3 ± 0.4 for the investigated gases. The loss of permeability of the modified LDPE films is the result of the nearly even fall of S and D . The values of P and D for the unmodified LDPE films given in Table 2 are in pretty good agreement with those reported earlier for LLDPE.³⁴

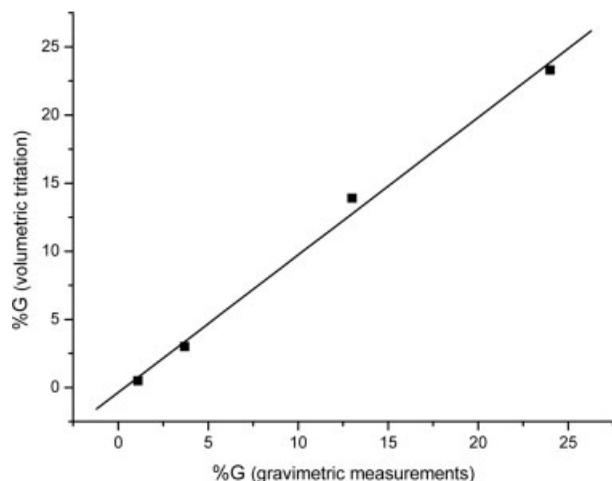


Figure 4. Correlation between the grafting percentages (%G) of poly(acrylic acid) onto polyethylene obtained by gravimetry and volume titration techniques.

DISCUSSION

The morphological effects of chemical grafting have been investigated with AFM, a powerful technique that allows the monitoring of the surface graft topography. Figure 6 shows AFM micrographs of LDPE and modified LDPE films with 3.7% poly(acrylic acid) grafting. The average values of the heights of the rugosity of the surfaces of unmodified and modified films are 209 and to 360 nm, respectively. It is expected that the grafting will preferably occur in the amorphous regions of the surface of the polyethylene films. At short times, brushes of poly(acrylic acid) attached to the surface of LDPE films presumably are formed. As time increases, cross reactions between grafted growing chains, as well as entanglements between chains of different brushes, form a network in which more linking between the network chains further occurs. Inhomogeneous domains covering the surface of the films grow as the grafting time increases, as micrographs not included here for different grafting percentages suggest.³² A central question in condensed matter physics is the length scale on which the molecular fluctuations of a liquid take place and under which conditions the transition from single-molecule behavior to that of a liquid occurs. This important issue was investigated by Huwe et al.³⁵ in a molecular dynamics study of liquids in confining space carried out by the combination of simula-

tions and broad-band dielectric spectroscopy. With ethylene glycol guest molecules confined to zeolite host systems of different topologies, they proved that a molecular arrangement of an ensemble as small as six molecules is enough to exhibit the dynamics of a bulk liquid. Considering that the thickness of the layer is several times the size of the mean square root of a high-molecular-weight (200,000) poly(acrylic acid) and taking into account Huwe et al.'s findings, one can postulate that the dynamics of the poly(acrylic acid) layer is similar to that of the bulk polymer. This fact suggests the glassy nature of the grafted poly(acrylic acid) layer.

The hydrophilic character of both the solvent and acrylic acid, on the one hand, and the relatively short reaction time, on the other hand, lead one to expect that grafting occurs only on the surface of the hydrophobic films. Then, the grafted polyethylene film can be viewed as a sort of laminate formed by a layer of poly(acrylic acid) covalently attached to the polyethylene film. The drop in pressure (Δp) across the laminate is

$$\Delta p = \Delta p_E + \Delta p_A \quad (7)$$

where Δp_E and Δp_A are the decreases in the gas pressure across the polyethylene film and the poly(acrylic acid) layer, respectively. Under

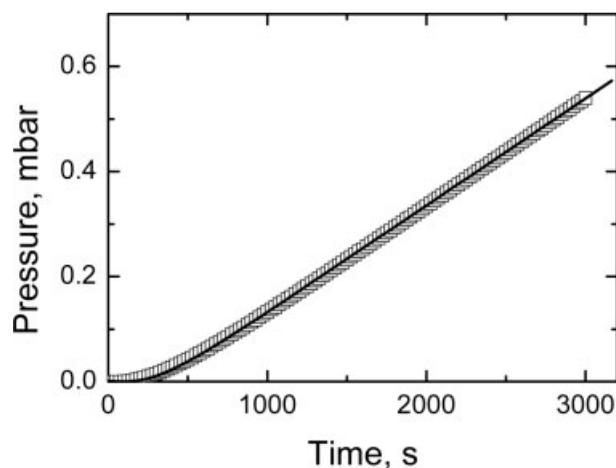


Figure 5. Illustrative plots showing the variation of the pressure of propane with time in the downstream chamber for a modified (grafting percentage = 3.7%) LDPE film. The continuous line represents the time dependence of the downstream pressure as calculated from the integration of Fick's second law with appropriate boundary conditions.

Table 2. Values at 30 °C of P and D of Different Gases for Modified (Grafting Percentage = 3.7%) and Unmodified LDPE Films at 1 bar

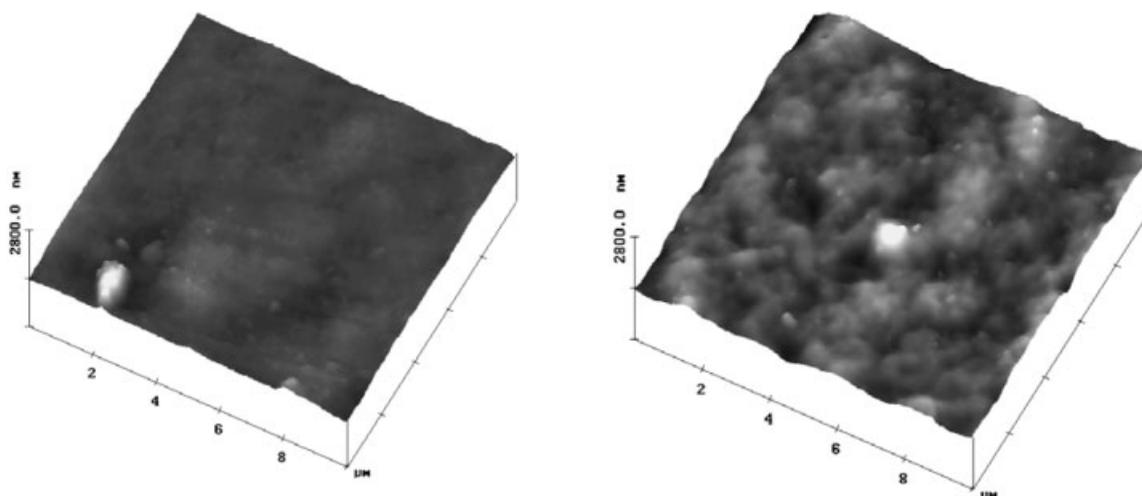
Gas	Unmodified LDPE Film			Modified LDPE Film		
	P (barrer)	$10^7 \times D$ (cm ² /s)	$10^3 \times S$ [cm ³ (STP)/ (cm ³ cmHg)]	P (barrer)	$10^7 \times D$ (cm ² /s)	$10^3 \times S$ [cm ³ (STP)/ (cm ³ cmHg)]
O ₂	2.60	5.60	0.46	0.45	2.09	0.22
N ₂	0.88	4.21	0.21	0.15	1.62	0.09
CO ₂	9.76	3.33	2.93	1.95	1.15	1.70
CH ₄	2.62	2.28	1.15	0.38	1.17	0.33
C ₂ H ₆	5.32	0.66	8.05	0.75	0.29	2.59
C ₂ H ₄	5.26	1.01	5.20	0.79	0.43	1.85
C ₃ H ₈	7.35	0.31	24.15	0.99	0.13	7.85
Ar	2.56	3.69	0.69	0.37	2.02	0.18
CO	1.37	3.09	0.44	0.20	1.98	0.10

steady-state conditions, Fick's first law holds, and eq 7 leads to

$$\frac{1}{P} = \frac{l_E}{l} \frac{1}{P_E} + \frac{l_A}{l} \frac{1}{P_A} \quad (8)$$

where l , l_E , and l_A represent the thickness of the grafted film, the unmodified film, and the poly(acrylic acid) layer, respectively, whereas the P parameters refer to the respective permeability coefficients. The average value of l_A can be estimated from $l_A = 0.037(\rho_E/\rho_A)l_E$, where ρ_E and ρ_A are the densities of the unmodified polyethylene and poly(acrylic acid) layer, respectively. This expression, in conjunction with eq 8,

allows a rough estimation of the P values of gases in the poly(acrylic acid) layer. The rearrangement of eq 8, assuming $l_E \approx l$ and taking into account that the permeability of the gases in the unmodified polyethylene is roughly six times that in the modified film, leads to $(P/P_A) \cong (l/l_A)[1 - (P/P_E)] = (5/6)(l/l_A)$. This indicates that the ratio of the P value of a gas in the modified polyethylene to that of the poly(acrylic acid) layer is independent of the nature of the gas. The fact that P/P_A is 29.2 ± 0.7 leads us to conclude that the poly(acrylic acid) layer largely controls the gas permeation through the modified films. To check the reliability of the values of P_A obtained from eq 8, we have tried to mea-


Figure 6. AFM micrographs for LDPE (left) and modified (grafting percentage = 3.7%) LDPE (right)

sure the permeability of poly(acrylic acid) films. However, this task presents serious difficulties. Polyacrylic films prepared via casting from water solutions contain a great number of bubbles, and besides that, the cast films are extremely brittle, thus impeding the measurement of gas transport across them with pressure gradient techniques. To circumvent this problem, sorption measurements of ethylene in a small piece of a poly(acrylic acid) film, without bubbles, were performed with a Cahn balance. The values of $3.4 \times 10^{-3} \text{ cm}^3 \text{ (STP)/cm}^3 \text{ cmHg}$ and $1.3 \times 10^{-7} \text{ cm}^2/\text{s}$ obtained for S and D of ethylene in poly(acrylic acid) yield $P = 4.4$ barrer. The relatively high permeability of ethylene across poly(acrylic acid) does not explain the sharp drop observed in gas permeation across the modified polyethylene films, unless the chains in the poly(acrylic acid) layer are highly crosslinked. In this case, chain fluctuations that give rise to the formation of nonpermanent channels through which the diffusant slips from a cavity to a nearby one would be severely restricted, and D would undergo a big decrease. Another possibility is that crystalline order develops in the layers during the grafting process, although X-ray diffractograms of modified and unmodified films do not show significant differences between them as one would expect because of the low grafting percentage of poly(acrylic acid) on the films. Although the development of crystallinity in poly(acrylic acid) seems to be unlikely because of the asymmetry of poly(acrylic acid), Makimoto et al.³⁶ reported that the polymerization of both butyl and methyl acrylate with heterogeneous organometallic compound catalysts gives amorphous polymers that after hydrolysis yield crystalline poly(acrylic acid). In view of this, further work is necessary to assess the nature of the poly(acrylic acid) layer of the modified films.

The pressure dependence of the transport properties of the most condensable gas, propane, across the modified LDPE film containing 3.7% grafted poly(acrylic acid) is shown in Table 3. P increases with pressure, whereas the value of D remains nearly constant. In fact, the average value of $10^8 \times D$ is $1.3 \pm 0.1 \text{ cm}^2/\text{s}$ in the pressure range of 0.18–3.76 bars, whereas the apparent value of $10^3 \times S$ rises from 5.70 to 11.10 $\text{cm}^3 \text{ (STP)/cm}^3 \text{ cmHg}$. The apparent values of S/ϕ , where ϕ represents the volume fraction of LDPE in the films, nearly coincide with Henry's solubility constant (k_{Da}) in the amorphous phase of

Table 3. Variation of the Gas-Transport Characteristics of Propane with Pressure in Surface-Modified (Grafting Percentage = 3.7%) LDPE Films at 30 °C

Pressure (bar)	P (barrer)	$10^8 \times D$ (cm^2/s)	$10^3 \times S$ [$\text{cm}^3 \text{ (STP)/}$ $(\text{cm}^3 \text{ cmHg})$]
0.18	0.83	1.46	5.70
0.35	0.86	1.34	6.43
0.63	0.89	1.29	6.94
1.03	0.99	1.26	7.85
2.10	1.13	1.27	8.91
2.93	1.22	1.25	9.75
3.76	1.40	1.26	11.10

LDPE. According to the theory, k_{Da} is related to thermodynamic parameters by^{37,38}

$$k_{\text{Da}} = \lim_{p \rightarrow 0} S_p = [22,414/(76\bar{V})] - \{(1 + \chi) - [(\lambda/RT_b)][1 - (T_b/T)]\} \quad (9)$$

where \bar{V} is the partial molar volume of the gas in the liquid state, R is the gases constant, T_b is the boiling temperature of the gas in the liquid state under 1 atm at working temperature T , λ is the latent heat of vaporization, and χ is the gas–polymer interaction parameter. The values of \bar{V} , T_b , and λ for different gases^{39,40} are given in Table 4. Earlier studies suggest that eq 9 also gives a good account of Henry's constant for glassy systems.^{41,42} The results for k_{Da} shown in the fifth and seventh columns of Table 4 for the unmodified and modified films, respectively, in conjunction with eq 9, lead to the values of χ shown in the sixth and eighth columns of Table 4. The less condensable gases exhibit higher gas–polymer repulsive interactions, and these interactions decrease as T_b increases, with χ reaching the lowest value for propane. The variation of χ with T_b is similar for surface-modified LDPE, although in this case the values of χ are slightly higher.

Under the assumption that gas diffusion is a random walk process, D is given by⁴³

$$D = v\lambda^2/6 \quad (10)$$

where v is the jumping frequency of the diffusant between neighboring holes and λ is the average jumping length. The jumping process from a hole or cavity to a neighboring one is carried out through nonpermanent channels formed by

Table 4. Values at 30 °C of λ , T_b , and \bar{V}^a

Gas	λ (kcal/mol) ^b	T_b (K) ^b	\bar{V} cm ³ / mol ^c	$10^3 \times k_{Da}$ (cm ³ /cm ³ cmHg)	χ	$10^3 \times k_{Da}^*$ (cm ³ /cm ³ cmHg)	χ^*
N ₂	1.330	72.4	35	0.32	2.14	0.14	2.99
O ₂	1.631	90.2	28	0.71	2.22	0.34	2.96
CO	1.444	81.7	35.4	0.68	1.93	0.15	3.41
CO ₂	4.112	194.7	46	4.52	2.46	2.62	3.00
CH ₄	1.944	111.7	38	1.77	1.86	0.51	3.11
C ₂ H ₆	3.50	185.0	55	12.42	1.36	4.00	2.49
C ₂ H ₄	3.23	169.5	49.3	8.02	1.39	2.85	2.42
C ₃ H ₈	4.477	231.1	76	33.10	1.45	12.11	2.45

^a Parameters k_{Da} and k_{Da}^* are Henry's constants referenced to 1 cm³ of the amorphous polymer for the unmodified and modified (grafting percentage = 3.7%) LDPE films, respectively, whereas χ and χ^* are the respective gas-polymer enthalpic parameters.

^b Reference 39.

^c Reference 40.

chain fluctuations, the walls of which are formed by the segments of the polymer matrix. The radius of the channels should be at least equal to the van der Waals radius of the diffusant (σ), so the activation energy associated with the diffusion process should be proportional to σ^2 . In this case,^{44,45} $D \sim \exp(-\sigma^2)$, or $\ln D \sim -\sigma^2$, and the plot of $\ln D$ versus σ^2 should be a straight line of a negative slope. The size of the gas molecules can be estimated from the Lennard-Jones collision diameter (σ_c), determined on the basis of the molecular interactions of a gas, and from the kinetic diameter, which is close to the molecular sieving dimension of the molecule.^{46,47} Collision and kinetic diameters are widely accepted correlation parameters for diffusivity in the rub-

bery and glassy states, respectively. The values of the natural logarithm of D of O₂, N₂, CO, Ar, CO₂, CH₄, C₂H₄, C₂H₆, and C₃H₈ through modified and unmodified films, represented as a function of the square of the collision diameter in Figure 7, roughly fit a straight line. The straight line for the modified LDPE lies below that of the unmodified one, presumably because the larger cohesive energy density of poly(acrylic acid) makes it more difficult to form a channel through which the diffusant can slide to a nearby hole in this latter polymer than in LDPE.

The temperature dependence of P and D of the gases for the surface-modified films is shown in Figure 8, whereas the pertinent activation

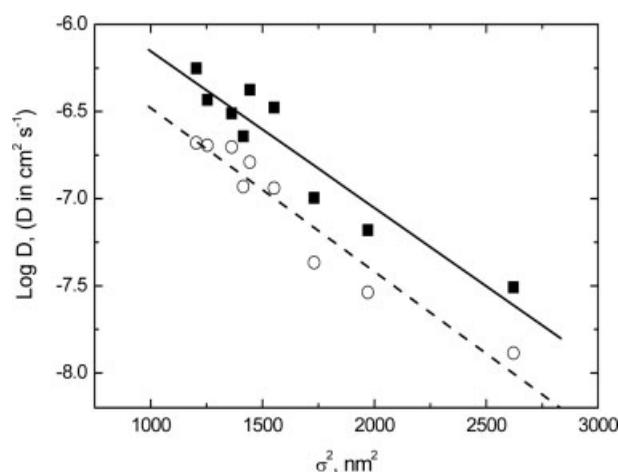


Figure 7. Dependence of the logarithm of the diffusion coefficient ($\log D$) on the square of the collision parameter (σ^2) of the gases for (■) LDPE and (○) modified (grafting percentage = 3.7%) LDPE.

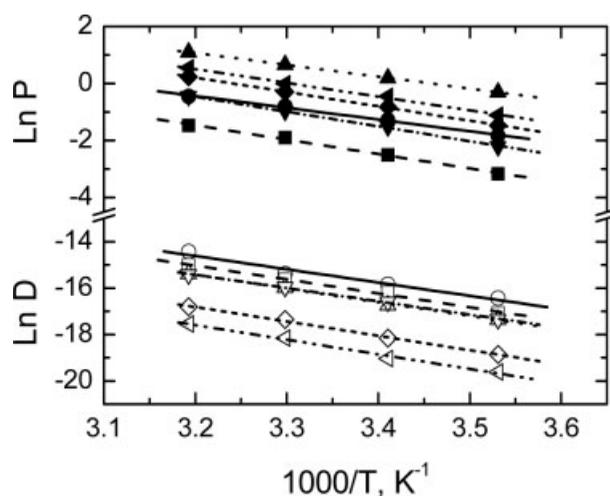


Figure 8. Arrhenius plots for D (open symbols) and P (filled symbols) of the following gases: (●,○) oxygen, (■,□) N₂, (▲,△) CO₂, (▼,▽) CH₄, (◆,◇) C₂H₆, and (◄,◃) C₃H₈.

Table 5. Values of E_P , E_D , and ΔH_S for Different Gases in Surface-Modified (Grafting Percentage = 3.7%) LDPE Films

Gas	E_P (kcal/mol)	E_D (kcal/mol)	ΔH_S (kcal/mol)
O ₂	8.2	11.5	-3.3
N ₂	10.1	12.0	-1.9
CO ₂	8.3	11.8	-3.5
CH ₄	10.4	11.4	-1.0
C ₂ H ₆	10.0	12.4	-2.4
C ₃ H ₈	9.6	12.6	-3.0

energies are given in Table 5. The values of the activation energy associated with the permeability coefficient (E_P) of the gases lie between 8.2 kcal/mol for oxygen and 10.4 kcal/mol for methane. This small variation in the activation energy is also observed in the case of the diffusion coefficient; the activation energy of the diffusive process (E_D) varies between 11.5 kcal/mol for oxygen and 12.6 kcal/mol for propane. The van't Hoff sorption heat (ΔH_S) can be obtained from E_P and E_D as follows:

$$S = \frac{P}{D} = \frac{P_0 \exp(-E_P/RT)}{D_0 \exp(-E_D/RT)} \quad (11)$$

On the other hand, the temperature dependence of S can be written as

$$S = S_0 \exp(-\Delta H_S/RT) \quad (12)$$

Obviously, $\Delta H_S = E_P - E_D$ as the comparison of eqs 11 and 12 shows. The values of ΔH_S are given in the fourth column of Table 5. For the homologous series of hydrocarbons and CO₂, the values of ΔH_S lie between -1.0 kcal/mol for methane and -3.5 kcal/mol for CO₂.

With the aim of investigating the effect of the asymmetry of the modified membranes on gas transport, permeation experiments were performed with the unmodified side of the membrane facing the upstream chamber. In general, the P value obtained with this configuration agrees very satisfactorily with that measured in the other way. For example, the values of P for oxygen, ethylene, and propane, at 30 °C, are 0.45, 0.77, and 0.97 barrers, respectively, in very good agreement with those obtained for the configuration with the modified surface facing the upstream chamber, which amount to 0.45, 0.79, and 0.99 barrers. As for D , the values of

$10^7 \times D$ are 2.40, 0.45, and 0.14 for oxygen, ethylene, and propane, respectively, in one of the configurations, and 2.09, 0.43, and 0.13, respectively, in the other configuration. Because similar behavior was found for the other gases, it can be concluded that gas transport is not affected by the asymmetry of the surface-modified LDPE films.

Let us briefly comment on the effect of the surface modification on the gas permselectivity of the films. The permselectivity of gas A with respect to gas B, $\alpha(A/B)$, is currently expressed as

$$\alpha(A/B) = \frac{P_A}{P_B} = \frac{D_A S_A}{D_B S_B} \quad (13)$$

Comparative values of the permselectivity coefficient for different pairs of gases are given in Table 6. The modification of the surface of the LDPE films slightly affects their permselectivity. The preference toward CO₂ over the other gases is somewhat higher in the case of the modified films.

Finally, it is worthwhile to compare the permeation characteristics of the modified films discussed in this work with those reported for membranes prepared from polyethylene-poly(acrylic acid) ionomers.²³ The permeation characteristics of the latter membranes depend on the concentration of ionic groups in the bulk. The P values at 30 °C for membranes containing 15% (w/w) acrylic acid are 0.67, 2.57, and 10.27 barrers for nitrogen, oxygen, and carbon dioxide, respectively, nearly four times larger than those found for the same gases in the surface-modified LDPE films. In general, the permeation characteristics of the membranes for different ionomers fractions come close to those reported in this study for LDPE. This fact suggests that the hydrophilic poly(acrylic acid) domains exhibit

Table 6. Permselectivity of Pairs of Gases for LDPE and Surface-Modified (Grafting = 3.7%) LDPE Films

Permselectivity	LDPE	Modified LDPE
$\alpha(\text{O}_2/\text{N}_2)$	3.0	3.0
$\alpha(\text{CO}_2/\text{O}_2)$	3.8	4.3
$\alpha(\text{CO}_2/\text{N}_2)$	11.1	13.0
$\alpha(\text{CO}_2/\text{CH}_4)$	3.7	5.1
$\alpha(\text{CO}_2/\text{C}_2\text{H}_6)$	1.8	2.6
$\alpha(\text{CO}_2/\text{C}_2\text{H}_4)$	1.9	2.5
$\alpha(\text{CO}_2/\text{C}_3\text{H}_8)$	1.3	2.0

permeability similar to that of the hydrophobic polyethylene domains.

CONCLUSIONS

Modified LDPE films can easily be prepared by the grafting of small amounts of poly(acrylic acid) onto the surface of the films with UV radiation. The poly(acrylic acid) layer covering the surface of the films, even for low grafting percentages, reduces the permeation of the films by about 80%. Therefore, the surface modification of LDPE with poly(acrylic acid) may have interesting applications, such as food preservation in the packaging industry. Either the development of ordered structures in the grafted layer or the formation of highly crosslinked grafted chains, which severely reduce chain fluctuations, is responsible for the sharp fall observed in the permeation characteristics of the surface-grafted films. The permselectivity of the modified films to gas transport is similar to that of the unmodified LDPE films.

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