Thermodynamic Model for the Permeability of Light Gases in Glassy Polymers

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The permeability of light gases in a series of different glassy polymers is analyzed through a thermodynamic-based approach for solubility and diffusivity. The nonequilibrium thermodynamic model for glassy polymers describes the solubility of the different penetrants; diffusivity is given as the product of a mobility factor and a thermodynamic factor. The latter is predicted by the nonequilibrium lattice fluid thermodynamic model, while the mobility coefficient is determined using the experimental permeability data. For rather soluble penetrants (e.g., CO_2), a plasticization factor is also accounted for, considering the mobility to depend exponentially on penetrant concentration, as often observed experimentally. The model is able to describe accurately the experimental behavior in a simple and effective way, considering only two adjustable parameters. The mobility coefficient is found to depend on the penetrant size (critical volume) and on the fractional free volume of the polymer matrix, following rather general and reasonable correlations. © 2015 American Institute of Chemical Engineers *AIChE J*, 61: 2776–2788, 2015

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Introduction

The mechanism of sorption and diffusion of gaseous, vapor, or liquid penetrants in polymers of different nature is of great importance for many practical purposes in a variety of industrial applications, such as those based on membranes and barrier polymeric films,[1–5] among others. The complete knowledge of such phenomena and their mathematical description through appropriate models are fundamental for a proper understanding and for design purposes.

The permeability P_1 of a low molecular weight penetrant, species 1, through a polymeric membrane provides the rate of transport of the permeating molecules at steady state, and is defined as

$$P_1=\frac{\dot{N}_1\ l}{p_1^{\mathrm{u}}-p_1^{\mathrm{d}}} \tag{1}$$

in which $\dot{N}_1$ is the molar flux of species 1, through a polymer film of thickness l, under the driving force given by the difference in partial pressures between the upstream and downstream phases, $p_1^{\mathrm{u}}-p_1^{\mathrm{d}}$.

The characterization of penetrant permeability, together with solubility, is widely employed to evaluate the performance of different membranes in gas separation, and to compare the behavior of the different gaseous species. Under the usual conditions in which $p_1^{\mathrm{u}} \gg p_1^{\mathrm{d}}$, the separation factor α_{ij} turns out to be the ratio between the permeability of species i and species j, and represents the membrane selectivity.

In the case of rubbery polymers, gas permeability is often invariant with upstream pressure: no significant variations are indeed registered for both solubility and diffusivity coefficients, unless very high values of pressure and concentrations are reached. On the contrary, polymer systems below T_g present very peculiar behaviors, in which permeability P_1 shows a significant dependence on upstream pressure, following different trends as it can be constant with pressure, as is common for light gases and penetrants scarcely soluble in the polymer, it can also be a decreasing function of p_1^{u}, as frequently encountered for different penetrants in many glasses, or else it can be an increasing function of p_1^{u}, as in the case of highly soluble penetrants, able to produce a relevant swelling of the polymer matrix. A nonmonotonous behavior of permeability can also be observed, initially decreasing then increasing with upstream pressure, reaching a minimum value which is the so-called plasticization point.

Therefore, a proper description of transport behavior is of remarkable importance to adequately represent the experimental results, and a suitable (and possibly simple) model is required to account for all the different behaviors encountered, using the same framework.

Earlier approach described the transport of gases in glassy polymers based on the Dual Mode Sorption (DMS) model,[6] assuming the existence of two separate populations of penetrant molecules, one dissolved and one adsorbed in the microvoids thought to be present in the glassy phase, referred to as Henry and Langmuir sorption modes, respectively. The overall permeability is then obtained by assuming that both populations diffuse in parallel, with two diffusivity

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values independent of concentration, and allowing for different possible exchange mechanisms between the two populations.[7,8]

The DMS model proved to be effective in the representation of permeability for a variety of different polymer and penetrant pairs,[9–12] but only for the cases in which permeability is never increasing with penetrant pressure. Indeed, the model expression is not suitable to describe the transport behavior in which permeability is always increasing with pressure or the so-called plasticization behavior often observed at higher pressures when a minimum value of permeability is present followed by an increasing trend. For such cases, the DMS model would require the introduction of at least two further *ad hoc* parameters.[13,14]

The main limitations of the DMS approach are on one side in the failure to represent complex behaviors of penetrant solubility, such as sigmoidal-shaped isotherms[15,16] and, on the other side, in the resulting dependence of apparent penetrant diffusivity, obtained from the parallel diffusion of the two different populations of molecules considered. In addition, the use of DMS model often leads to a poor prediction of the time lag of diffusion, to the point that improvements to time lag description have been pursued even considering that the species adsorbed onto the surfaces of the holes can diffuse as such without any exchanges with the bulk, as if the holes were communicating with one other as in a continuous interconnected void phase.[17]

Alternative models have been developed over the past decades for the interpretation of the gas transport in glassy polymers. Petropoulos developed a different approach based on chemical potential gradient, within the same DMS framework,[18] but still considering the mobility value constant with concentration; similarly Islam and Buschatz[19] followed the same idea considering a pressure gradient inside the membrane, leading however to contradictory results.[20] Barbari developed a new model for the permeability of swelling penetrants, considering the dilation of a glassy polymer matrix within the dual mode model, and utilizing a free-volume model for the representation of the diffusion coefficient,[21] aiming at the description of the behavior of highly soluble penetrants. A different approach has been considered by Lee et al., who developed a thermodynamic model on the basis of configurational entropy and Flory–Huggins theory to evaluate the concentration dependence of gas permeability; but that can hardly be utilized for the study of polymeric systems with a significant fraction of free volume.[22]

All the mentioned models can provide a good description of the experimental results in certain limited ranges of operating conditions, but their validity is actually confined to special intervals and cannot be used to represent all possible behaviors, unless further additional terms and parameters are specifically introduced. Indeed, none of the models listed above is able to describe all the four different features usually encountered in penetrant transport in glassy polymers.

In this work, the permeability behavior of light gases in several glassy polymers is considered and analyzed by means of an approach recently proposed.[23] The simple and effective model introduced by Minelli and Sarti[23] for the evaluation of the permeability of gases in glassy polymers, based on only two adjustable parameters, has been already employed to model the different permeability behaviors of CO_2 in various glassy polymers,[23] as well as in polymer blends and copolymers,[24] describing with a very good accuracy all different permeability dependencies on upstream penetrant pressure. The case of different penetrants, as organic vapors, hydrocarbons and alcohols in glassy ethyl cellulose has also been successfully considered at different temperatures.[25,26] Furthermore, the model also represents accurately the temperature dependence of permeability and solubility of CO_2 in semicrystalline poly(ethylene terephthalate) (PET), below and above its T_g.[27]

Such an approach, whose details are illustrated in our previous work,[23] calculates the gas permeability in glassy polymers determining separately the two contributions, given by the average value of the diffusion coefficient $<D_1>$, in the concentration range of interest i.e., between the values at the upstream and downstream polymer interfaces, c_1^u and c_1^d, respectively, and the average solubility coefficient $<S_1>$ defined as

$$<S_1> = \frac{c_1^u - c_1^d}{p_1^u - p_1^d} \tag{2}$$

From the average solubility and diffusivity coefficients, the determination of the steady-state permeability is straightforward, and in case the downstream pressure is negligibly small with respect to the upstream value (i.e., $p_1^d \simeq 0$ and consequently $c_1^d \simeq 0$), the following equation holds true

$$\lim_{p_1^d \to 0} < D_1 > = \lim_{p_1^d \to 0} \frac{\dot{N}_1 l}{c_1^u} = \frac{P_1 p_1^u}{c_1^u} = \frac{P_1}{<S_1>} \tag{3}$$

The model considers the diffusion coefficient as the product of a purely kinetic factor, the mobility coefficient L, and a thermodynamic factor $\alpha = \frac{\partial \mu_1}{\partial \ln \omega_1}$, with ω_1 the mass fraction of penetrant species 1. The latter factor is associated to the concentration dependence of the chemical potential of the permeating species, and can be evaluated directly from the experimental solubility isotherm, or from a specific model for the penetrant solubility.

The mobility coefficient is in general depending on penetrant concentration, and an exponential dependence on ω_i is found appropriate for quite soluble penetrants, such as CO_2 or hydrocarbons.

Conversely, the description of the solubility isotherms of the different penetrants is provided by the use of nonequilibrium thermodynamic theory for glassy polymers[28,29] which gives rise to the nonequilibrium lattice fluid (NELF) model,[30,31] when applied to the Sanchez Lacombe equation of state (EoS).[32,33]

The resulting transport model[23] contains overall only two adjustable parameters, required to describe the dependence of penetrant mobility on penetrant concentration, and it is suitable to represent any kind of permeability behavior observed experimentally, even in case of strong plasticization phenomena.

The approach introduced in Ref. 23 represents a comprehensive framework for the description of gas permeability, which can be implemented also using any other solubility and mobility model. It offers a simple and solid model with strong theoretical basis, able to evaluate and possibly to predict the penetrant permeability, exploiting the thermodynamics of glassy polymer mixtures and a convenient representation of the penetrant mobility in that mixture. The model is not a mere correlation tool for an accurate fit of experimental data, but it rather provides a deeper understanding of mass transport in glassy polymers, valid in a broad range of operating conditions, and it is also able to provide useful information on the effect of polymer properties on membrane behaviors.

Table 1. Definition of the Different Properties as Well as Main Correlations for the Sanchez–Lacombe/NELF Framework

	Symbol	Name
State Variables	ω_i	Mass fraction of solute *i*
	T	Temperature
	p	Pressure
	ρ_2	Polymer mass density
Model Parameters	ρ_i^*	Characteristic density of pure component *i*
	p_i^*	Characteristic pressure of pure component *i*
	T_i^*	Characteristic temperature of pure component *i*
	M_i	Molar mass component *i*
	$k_{1,2}$	Binary interaction parameter for penetrant, polymer (1,2) pair

			Eq.	Calculation
Model Variables	v_i^*	Lattice site molar volume for pure component *i*	I	$v_i^* = \frac{RT_i^*}{p_i^*}$
	ρ^*	Characteristic density of the mixture	II	$\frac{1}{\rho^*} = \frac{\omega_1}{\rho_1^*} + \frac{\omega_2}{\rho_2^*}$
	$\tilde{\rho}$	Reduce mixture density	III	$\tilde{\rho} = \frac{\rho_2}{(1-\omega_2)\rho^*}$
	ϕ_i	Volume fraction of component *i* in the mixture	IV	$\phi_i = \omega_i \frac{\rho^*}{\rho_i^*}$
	v^*	Average close-packed per molar volume in the mixture	V	$\frac{1}{v^*} = \frac{\phi_1}{v_1^*} + \frac{\phi_2}{v_2^*}$
	Δp_{ij}^*	Interaction characteristic pressure for (1,2) pair in the mixture	VI	$\Delta p_{12}^* = p_1^* + p_2^* - 2(1-k_{12})\sqrt{p_1^* \cdot p_2^*}$
	$\mu_i^{\mathrm{NE,res}}$	Residual chemical potential of solute *i* in the glassy polymeric mixture	VII	$\frac{\mu_1^{\mathrm{NE,res}}}{RT} = \frac{M_1}{\rho_1^* v^*}\left\{1 - \frac{v_1^*}{v^*} - \ln(1-\tilde{\rho})\left[1 - \frac{1 - v_1^*/v^*}{\tilde{\rho}}\right] - \tilde{\rho} v_1^*\left[(1+\phi_1)p_1^* + \phi_2\left(p_2^* - \Delta p_{1,2}^*\right)\right]\right\}$

In the present work, we inspect the application of that model to describe the permeation data of light gases, such as nitrogen, argon, or helium, which were not yet considered so far. Such penetrants induce a very limited swelling in the polymer matrix in view of their moderate solubility, and thus they are not able to produce any significant plasticization in the polymer matrix. Therefore, the values of mobility coefficient for light gases are expected to be approximately constant throughout the whole pressure range usually considered.

Theoretical Background

The transport model developed by Minelli and Sarti has been already widely described in previous publications,[23,24] and only its main features are here recalled for clarity sake.

The penetrant permeability in glassy polymers requires the determination of both solubility and diffusivity coefficients. The first, S_1, is readily obtained from EoS-based model specifically devoted to the case of glassy phases (e.g., NELF model), while the second coefficient D_1, is considered as the product of two factors, and for the case of binary penetrant/polymer mixtures, the following relation holds

$$D_1 = \frac{\partial \mu_1 / RT}{\partial \ln \omega_1} \cdot L_1 \equiv \alpha \cdot L_1 \tag{4}$$

in which ω_1 is the penetrant mass fraction, L_1 is the kinetic mobility of penetrant 1, and the thermodynamic factor α is defined in Eq. 4.

The thermodynamic factor can be determined from the specific expression of chemical potential in binary mixtures provided by the NELF model, whose relevant physical quantities and equations are summarized in Table 1. The NELF model requires the use of pure polymer and penetrant characteristic parameters, a binary interaction coefficient k_{12}, and the value of the specific volume of the glassy polymer at the various penetrant pressures. The description of the volumetric dilation of the polymer, when present, is provided in a predictive fashion by the approach by Minelli and Doghieri.[34] Therefore, the thermodynamic factor α is obtained in purely predictive manner, once the only binary factor k_{12} is retrieved from the analysis of a limited set of experimental solubility data.

Conversely, also the mobility coefficient often reveals a non-negligible dependence on penetrant concentration, especially for highly plasticizing penetrants, so that in the previous works an exponential relationship has been considered[23–27]

$$L_1(\omega_1) = L_{10} \cdot e^{\beta \omega_1} \tag{5}$$

in which L_{10} is the infinite dilution mobility coefficient and β is the plasticization factor, associated to the penetrant/polymer pair under consideration. Other more elaborate expressions are clearly available for the penetrant mobility, such as those derived within the free volume theory by Vrentas and Duda[35]; if necessary, they could also be easily implemented in the present modeling procedure. However, in all the cases considered thus far Eq. 5 was found sufficient for all purposes and, therefore, this expression will be considered also in the present work, in which the attention is focused in particular on the permeability of light gases.

The model then requires an accurate and reliable representation of the thermodynamic properties of the penetrant/polymer mixture below T_g, to calculate the thermodynamic factor and the penetrant solubility at the various pressures. The NELF model is thus employed to that aim, in view of its

Table 2. Characteristic Parameters of Pure Polymer and Penetrant Substances of the Sanchez Lacombe/NELF Model

	T^* (K)	p^* (MPa)	ρ^* (g/cm^3)	Source
CO_2	300	630	1.515	28
CH_4	215	250	0.500	31
C_2H_4	295	345	0.680	31
Ar	190	180	1.400	36
N_2	145	160	0.943	31
He	9.3	4.0	0.148	36
PC	755	534	1.275	28
PSf	820	560	1.318	28
PMMA	695	560	1.270	31
PVC	680	620	1.487	This work, data from Ref. 37
PEMA	602	567	1.221	38
PPO	739	479	1.177	38

recognized ability to provide the full thermodynamic representation of polymer solutions in the glassy state. The detailed description of this model can be found in previous papers[28,30,31]; its main features and final results are here briefly recalled for the sake of clarity.

It was shown[28,30,31] that the use of the actual value of the nonequilibrium polymer density, ρ_2^{NE}, as a measure of the departure from equilibrium of the glassy phase, provides a good and general description of the thermodynamic state of the system, together with the usual set of state variables (temperature, pressure, and mass fraction). The NELF model adopts the lattice fluid framework (LF) given by Sanchez and Lacombe,[32,33] and thus represents the pertinent extension of the EoS approach to the glassy region. The definition of the model parameters and the equations used in the NELF model (and in the Sanchez Lacombe theory) are summarized in Table 1. The properties of the pure polymers and pure penetrants are determined on the basis of the three characteristic parameters (T_i^*, p_i^*, and ρ_i^*) of the EoS, whose values are obtained from the best fit of pressure-volume-temperature (pVT) data or from vapor-liquid-equilibrium data. In the present case, the polymers and the penetrants investigated have been already analyzed either by the Sanchez Lacombe EoS or by the NELF model, and thus their characteristic parameters, reported in Table 2, are already available in the literature.

The properties of the penetrant/polymer mixtures are obtained by the mixing rules for the LF theory,[32,33] which are also reported in Table 1.

The behavior of penetrant solubility at various solute pressures or activities can thus be obtained from phase equilibrium calculations, in which the chemical potential of the penetrant sorbed in the polymer phase, μ_1^{NE}, is equal to that in the external fluid phase $\mu_1^{Eq,ext}$

$$\mu_1^{NE}\left(T,p,\omega_1,\rho_2^{NE}\right)=\mu_1^{Eq,ext}(T,p,y_1) \qquad (6)$$

As input parameter, the NELF model requires the knowledge of the glassy polymer density, ρ_2^{NE}, which must be obtained at all the different conditions inspected, that is, at the different temperatures, pressures, and solute fugacities. Conversely, the volume of a glassy polymer exposed to light gases is practically constant, at least in the usual limited pressure ranges, as the very small penetrant uptake does not produce any significant dilation of the penetrated matrix. However, Minelli and Doghieri have recently developed a specific method for the determination of the penetrant induced swelling,[34,39] which can be effectively evaluated in a purely predictive way by means of a simplified rheological approach.

This method is based on a bimodal distribution of the characteristic polymer relaxation times, considering only the short-term and long-term relaxation modes, associated to “soft” and “hard” elements, respectively; their mass fractions, χ and $1-\chi$, respectively, are intrinsic characteristic property of the polymeric glass. The core of this approach is the assumption that only short-term relaxation phenomena are involved during sorption well below T_g, so that only the soft elements contribute to polymer swelling. Once pseudoequilibrium conditions are reached, the volume of the hard element remains unchanged, while the volume of the soft portion has reached the value corresponding to its hypothetical equilibrium state at that temperature, pressure, and solute mass fraction or fugacity. The χ factor thus represents the swellable polymer mass fraction, and the following equation holds[34]

$$\frac{1}{\rho_2^{NE}(T,p,f_1)}=\left(\frac{1}{\rho_{20}^{NE}}\right)+\chi\left(\frac{1}{\rho_2^{Eq}(T,p,f_1)}-\frac{1}{\rho_2^{Eq}(T,p,0)}\right) \qquad (7)$$

in which the density of the polymer phase in the glassy state, ρ_2^{NE}, at temperature T, pressure p, and solute fugacity f_1, is evaluated based on the χ factor, the density of the polymer in the unpenetrated state ρ_{20}^{NE}, and the equilibrium density ρ_2^{Eq}, conveniently evaluated by suitable EoS.

The model parameter χ is estimated on the basis of the volumetric data for pure polymer in both rubbery and glassy state; the following relation is thus derived[34]

$$\chi=\frac{\kappa_{g,2}\left(T_g^-\right)}{\kappa_{m,2}\left(T_g^+\right)} \qquad (8)$$

in which $\kappa_{g,2}$ and $\kappa_{m,2}$ indicate the isothermal compressibility of the polymer below and above the glass transition temperature, respectively, evaluated at the glass transition temperature for the polymer of interest.

Table 3. Characteristic Parameters of the Different Polymers: Initial Unpenetrated Polymer Density and χ Factor

Polymer	ρ_{20}^{NE} (g/cm^3)	χ
PC	1.194	0.69
PPO	1.063	0.46
PEMA	1.122	0.83
PSf	1.235	0.56
PVC	1.367	0.81
PMMA	1.175	0.69

Table 4. Penetrant/Polymer Binary Interaction Coefficients for the Sanchez Lacombe/NELF Model

Polymer	Penetrant	k_{12}	Polymer	Penetrant	k_{12}
PC	CO_2	0.022	PSf	CO_2	0.013
	CH_4	0.035		CH_4	0.015
	C_2H_4	0.009		Ar	0.045
	Ar	0.030		N_2	−0.020
	N_2	−0.018		He	−1.00
	He	−1.010	PVC	CO_2	0.080
PPO	CO_2	−0.007		CH_4	0.142
	CH_4	−0.057		Ar	0.206
	Ar	0.052		N_2	0.210
	N_2	0.020		He	−0.531
PEMA	CO_2	0.025	PMMA	CO_2	0.006
	CH_4	0.017		CH_4	0.055
	Ar	0.061		Ar	0.100
	N_2	0.032		N_2	0.055
				He	−2.94

The estimation of solute induced swelling is fundamental for the proper description of the solubility in glassy polymers of highly swelling penetrants, such as CO_2 or C_2H_4 among those here considered, while in case of light gases as N_2 or He, almost negligible dilations are predicted by the present model; intermediate behaviors are often found for CH_4 or Ar. For the sake of consistency, in this work all different cases will be equally treated by the same approach illustrated above: accordingly, polymer swelling will be determined predictively and used as input to the NELF model to describe the thermodynamic behavior below T_g.

The final expression for penetrant permeability can then be derived by taking advantage of Eq. 4 for diffusivity, of Eq. 5 for mobility, and of the results of the NELF model for the thermodynamic factor α and for the solubility coefficient, $S_1 = \frac{\omega_1}{p_1}$. In the case of negligible penetrant pressure in the downstream side of the membrane, the following relationship holds[23]

$$P_1 = \frac{1}{M_1 p_1^{\mathrm{u}}} \int_0^{p_1^{\mathrm{u}}} \rho_2 \; L_{10} \exp\left(\beta \omega_1\right) \; \frac{\omega_1}{p_1} \; z_1 \; dp_1 \tag{9}$$

where M_1 is the penetrant molecular weight, p_1^{u} is the penetrant upstream pressure, and z_1 is its compressibility factor, which can be evaluated through the Peng–Robinson EoS, for the sake of convenience. Of course, any other suitable model, including the same lattice fluid EoS, can be used for this purpose observing only very minor differences in the final results.

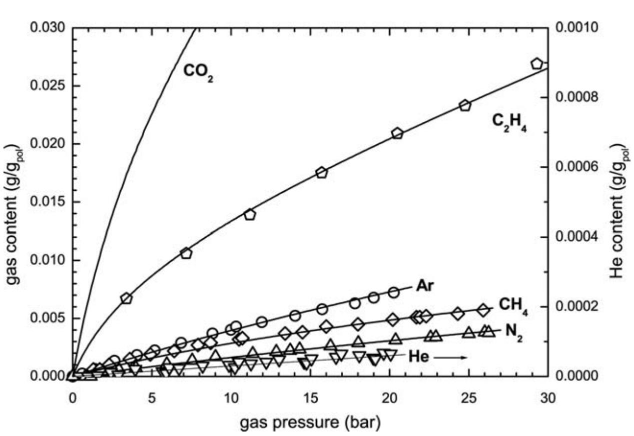

Figure 1. **Gas solubility isotherms in glassy polycarbonate at 35°C: experimental data after Koros et al.[40] and Jordan and Koros,[41] together with the NELF model results.**

Results

The approach described above has been applied to a variety of different cases to represent the permeability behavior of the different light penetrants in glassy polymers. Particular

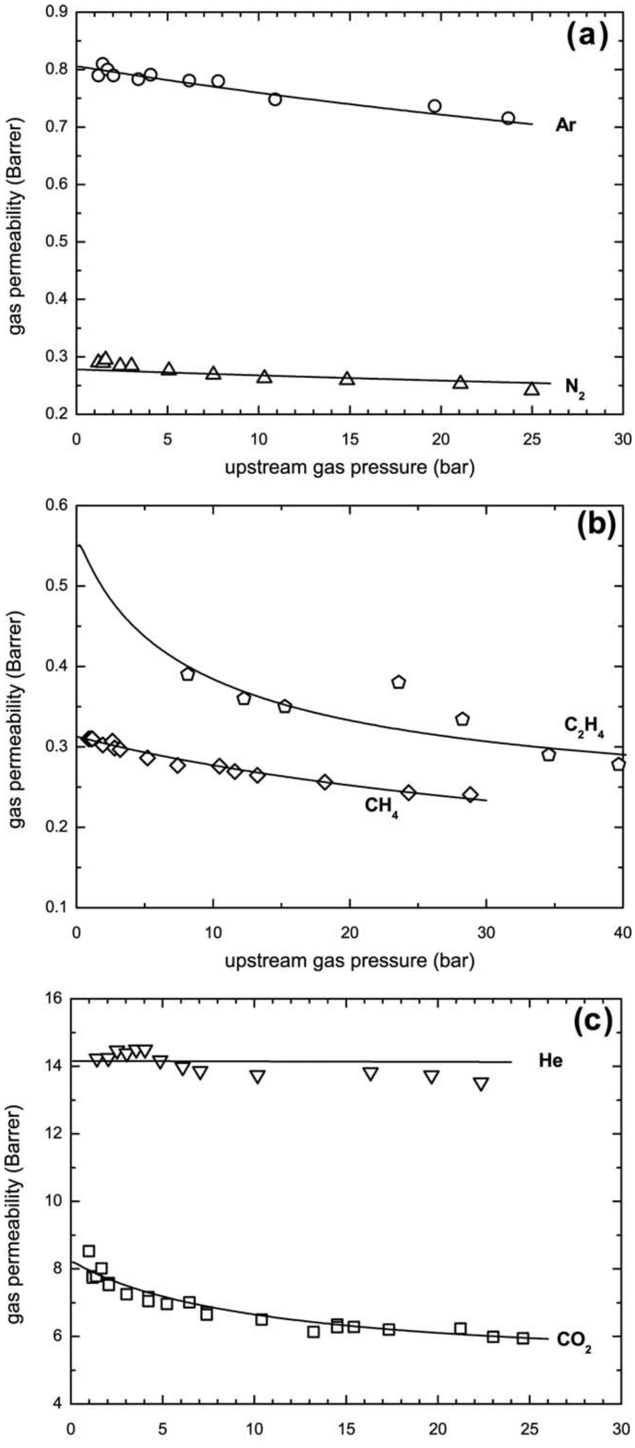

Figure 2. **Gas permeability isotherms in glassy polycarbonate at 35°C: experimental data after Koros et al.[40] and Barbari,[21] together with the transport model results.**

attention has been here devoted to the permeation of light gases such as N_2, CH_4, and also Ar, He, or C_2H_4, whenever the experimental data are available. CO_2 solubility and permeability curves, already analyzed in a previous work,[23] have also been reported for the sake of comparison.

The NELF model can provide the solubility isotherms in a simple and straightforward way, once the equilibrium and nonequilibrium parameters ρ_{20}^{NE} and χ are properly determined. The polymer density in dry conditions, ρ_{20}^{NE}, is determined from specific volumetric data collection,[37] while the χ factor is obtained from previous analyses[34,39]; such values are reported in Table 3.

The binary interaction parameters, k_{12}, of the Sanchez Lacombe EoS can be evaluated from independent equilibrium data above T_g. Alternatively, as in most cases that information is not experimentally available, k_{12} can also be estimated from the best fit of the NELF model to the solubility behavior of the penetrant in the glassy polymer phase. In this work, this latter procedure was used for most penetrants but CO_2, whose parameters, on the contrary, were retrieved from equilibrium data above T_g, as reported in a previous publication.[34] The resulting values of binary interaction parameters are included in Table 4.

Gas solubility and transport in polycarbonate

The transport model has been first applied to the case of different gases in glassy polycarbonate, analyzing the experimental data of solubility and permeability obtained by Koros et al.[40] for CO_2, Ar, He, CH_4, and N_2, as well as by Jordan and Koros,[41] for C_2H_4.

Figure 1 reports the experimental solubility data of the different light gases in polycarbonate (PC) at 35°C, together with the NELF model curves; the behavior of CO_2, already analyzed in a previous work,[23] is also partially included for comparison. Clearly, the model gives an accurate description of the experimental data for all penetrants inspected, allowing thus the correct representation of the thermodynamic properties of the solute/polymer mixtures required by the transport model. The values of initial polymer density and compressibility factor, required as input parameter by the model, are obtained from the volumetric data reported by Zoller and Walsh[37] and from a previous work,[34] respectively; they are both reported in Table 3.

Interestingly, the experimental isotherms show the typical behavior for gases in glassy polymers, concave toward the pressure axis, with a solubility coefficient $\frac{\omega_1}{p_1}$ decreasing with pressure: this trend is apparent for CO_2 and C_2H_4, and less pronounced for Ar and CH_4, while, on the other hand, for N_2 and He the isotherms are practically linear. All such features are well described by the NELF model, by means of one binary parameter only, the equilibrium interaction coefficient k_{12}, with no need of additional nonequilibrium information.

The gas permeabilities in glassy PC are also significantly pressure dependent, and the experimental data report P_1 trends clearly decreasing with pressure, at least in the range investigated, approximately up to 30 bar,[21,40] as illustrated in Figures 2a–c. The decreasing slope is rather different for the different penetrants considered: strong decrements of P_1 are observed for CO_2, C_2H_4, and CH_4, whereas limited reductions in the range of only 10% or less are reported for Ar, N_2, and He.

All such features are well represented by the present transport model, which is able to accurately describe the experimental behaviors of all penetrants, based only on the two adjustable parameters retrieved from the best fit of the experimental data. The resulting values of infinite dilution mobility coefficient, L_{10}, and plasticization factor, β, are reported in Table 5.

Interestingly, a zero value of β is obtained for all the less condensable penetrants, N_2, Ar, and He, so that the whole permeability isotherms can be described simply by a constant mobility coefficient. That is consistent with the scarce solubility of these penetrants in glassy polycarbonate, which is not able to produce any significant plasticization of the polymer matrix. A small plasticization factor β was used for the case of CH_4, although that leads to a very small increase in L, from approximately 3.9×10^{-9} cm^2/s at infinite dilution, to 4.1×10^{-9} cm^2/s at the maximum pressure inspected (30 bar), corresponding to a CH_4 content in the polymer phase of 0.6 % g/g$_{\mathrm{pol}}$.

Gas solubility and transport in polysulfone

The same procedure is applied to the solubility and permeability behavior of different penetrants, CO_2, CH_4, N_2, Ar, and He, in glassy polysulfone (PSf) at 35°C, considering the experimental data reported by Erb and Paul.[42]

The solubility data are first analyzed by the NELF model, accounting for the prediction of the penetrant-induced swelling. Figure 3 compares the model results with the experimental solubility isotherms at 35°C in glassy polysulfone of Ar, CH_4, and N_2 by Erb and Paul,[42] and He by Smith

Table 5. Infinite Dilution Mobility Coefficients and Plasticization Factors for the Different Penetrant/Polymer Systems

Polymer	Penetrant	L_{10} (cm^2/s)	β	Polymer	Penetrant	L_{10} (cm^2/s)	β
PC	CO_2	1.3×10^{-8}	16.2	PSf	CO_2	9.0×10^{-9}	17.5
	CH_4	3.9×10^{-9}	9.0		CH_4	2.1×10^{-9}	0
	C_2H_4	1.3×10^{-9}	28.0		Ar	1.1×10^{-8}	0
	Ar	2.0×10^{-8}	0		N_2	6.4×10^{-9}	0
	N_2	1.2×10^{-8}	0		He	3.4×10^{-6}	0
	He	5.2×10^{-6}	0	PVC	CO_2	1.4×10^{-9}	28.0
PPO	CO_2	7.8×10^{-8}	12.8		CH_4	4.7×10^{-10}	0
	CH_4	1.9×10^{-8}	8.0		Ar	3.1×10^{-9}	0
	Ar	1.2×10^{-7}	3.0		N_2	1.8×10^{-9}	0
	N_2	9.4×10^{-8}	0		He	3.0×10^{-6}	0
PEMA	CO_2	2.3×10^{-8}	40.0	PMMA	CO_2	7.2×10^{-10}	42.5
	CH_4	1.1×10^{-8}	10.0		CH_4	8.1×10^{-11}	0
	Ar	6.0×10^{-8}	5.0		Ar	9.8×10^{-10}	0
	N_2	4.2×10^{-8}	0		N_2	6.5×10^{-10}	0
					He	2.4×10^{-7}	0

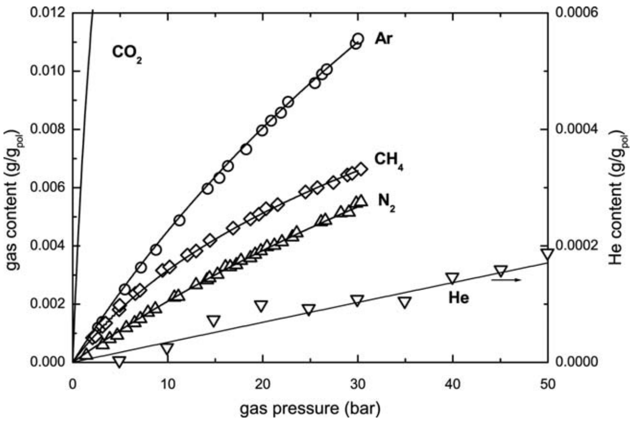

Figure 3. Gas solubility isotherms in glassy polysulfone at 35°C: experimental data after Erb and Paul[42] and Smith et al.,[43] together with the NELF model results.

et al.[43]; the curve obtained for CO_2, already analyzed in a previous work,[34] has been included for the sake of comparison.

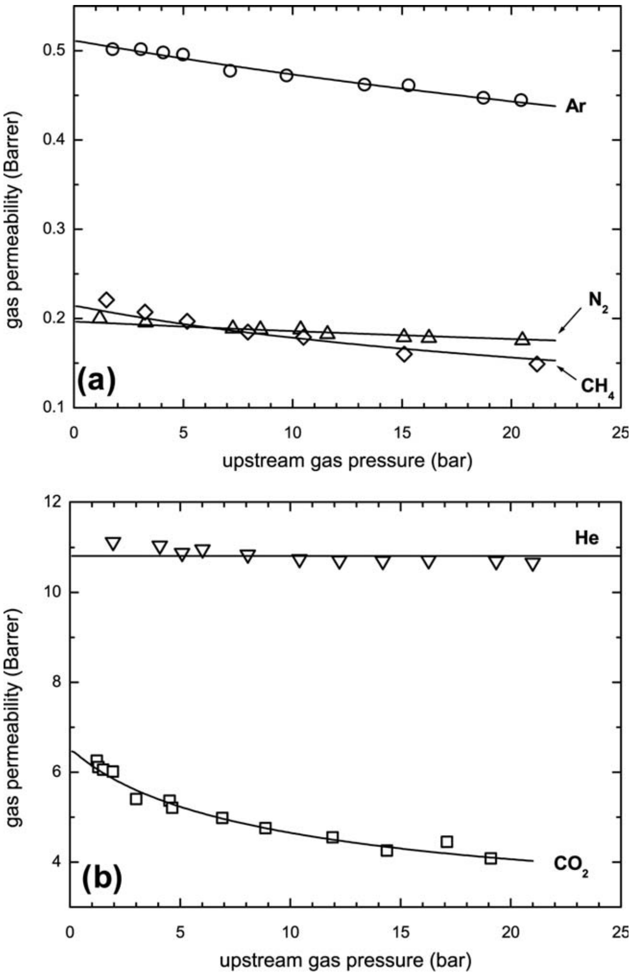

Figure 4. (a, b) Gas permeability isotherms in glassy polysulfone at 35°C: experimental data after Erb and Paul,[42] together with the transport model results.

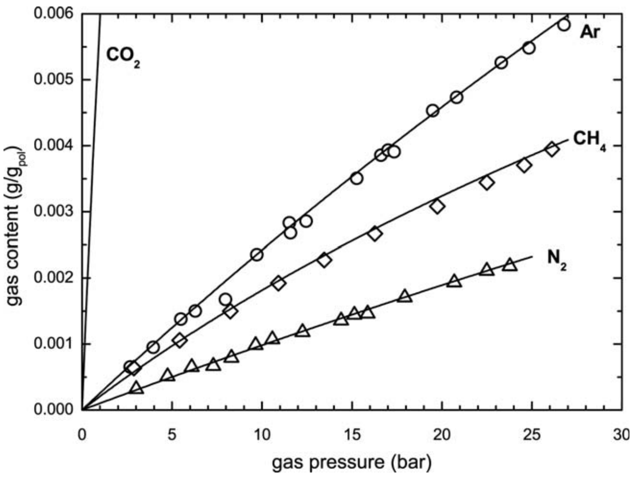

Figure 5. Gas solubility isotherms in glassy poly(methylmethacrylate) at 35°C: experimental data after Chiou and Paul,[45,46] together with the NELF model results.

No specific value of initial polymer density was reported in the original papers, so the value of 1.235 g/cm^3 has been considered for glassy polysulfone, according to what often reported in the literature.[44] The unpenetrated polymer density is reported in Table 3, together with the factor χ obtained in a previous work.[34] The binary interaction coefficients, k_{12}, for the different penetrants have been retrieved from the best fit of the experimental solubility data, and the resulting values are reported in Table 4. As apparent in Figure 3, the NELF model is able to represent very accurately the experimental solubility data.

The permeability isotherms of the different penetrants in glassy polysulfone are illustrated in Figures 4a, b, in which the experimental data by Erb and Paul[42] are reported together with the curves obtained by the present transport model.

The permeability isotherms of all penetrants show the decreasing trends with upstream pressure typical of many glassy polymers; furthermore, as in the case of polycarbonate, the extent of decrease is more pronounced for CO_2 and CH_4, than for N_2 or Ar, while helium permeability is practically constant up to 30 bar. The transport model applied is able to describe all the behaviors with a very good accuracy, using only one adjustable parameter, that is, the mobility L_{10}, throughout the whole pressure range, whose values are reported in Table 4. In all cases but CO_2, the experimental data can be represented by neglecting any effect of the penetrant concentration on the mobility coefficient, namely a zero plasticization factor is sufficient for CH_4, N_2, Ar, and He.

Gas solubility and transport in poly(methylmethacrylate)

The case of gas solubility and permeability in glassy poly(methylmethacrylate) (PMMA) is considered analyzing the sets of experimental data at 35°C reported by Chiou and Paul,[45,46] using CO_2, Ar, CH_4, N_2, and He as penetrants.

The experimental solubility isotherms of the different solutes are reported in Figure 5 together with the results of the NELF calculations, which show the very good accuracy of the model predictions, using k_{12} as the only adjustable parameter for each penetrant/polymer couple. The solubility of CO_2 is reported only for the sake of comparison. The NELF model provides the thermodynamic description of the solute/polymer systems below T_g, and the values of both dry polymer density and χ factor (reported in Table 3) are the

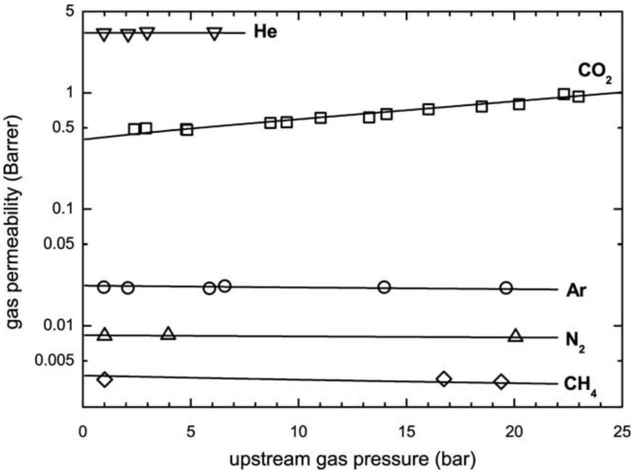

Figure 6. Gas permeability isotherms in glassy poly (methylmethacrylate) at 35°C: experimental data after Chiou and Paul,[45,46] together with the transport model results.

only input parameters required. The factor χ is obtained from a previous work,[39] while the value of ρ_{20}^{NE} is determined from the density measurement at 30°C included in the original paper,[46] and from the isothermal dilation coefficient resulting from Zoller and Walsh.[37]

As no experimental characterization of helium solubility has been found in the literature, the model analysis of the thermodynamic properties of He/PMMA system has been obtained by retrieving the binary interaction coefficient $k_{12} = -2.94$ from the single data point of solubility coefficient of He in PMMA above T_g, reported by Durill and Griskey at 188°C.[47]

The experimental transport properties of the different gases in PMMA at 35°C reported by Chiou and Paul[45,46] (Figure 6) showed a nearly constant light gas permeability with upstream penetrant pressure, and only a very slight decrease as penetrant pressure increases. Conversely, a clear increasing trend with penetrant pressure was observed for CO_2, as already discussed in a previous work.[23]

Such features are accurately represented by the transport model considered, which is able to provide a precise description of the permeability at the various penetrant pressures, on the basis of the solubility behavior of the different probes, and of the kinetic parameters considered. In view of the very limited solubility of the light gases examined, always well below 1 wt %, no plasticization of the polymer matrix takes place, and the whole permeability isotherms can be described by the same mobility coefficient, that is, the value of the plasticization factor β is zero for the light gases. The complete set of transport parameters for light gases in PMMA is reported in Table 5, together with those for CO_2, for the sake of comparison.

As expected, the resulting mobility coefficients are considerably lower than those in polycarbonate or in polysulfone, due to the more compact structure of PMMA in the glassy state, which results in the low gas solubility and mobility coefficients, particularly low for incondensable gases such as N_2 or Ar.[48] Conversely, CO_2 is quite soluble in PMMA in view of its positive interaction with the polymer, and it is thus able to induce a significant swelling of the matrix, eventually leading to a strong enhancement of the penetrant mobility, that is, to a large value of the plasticization factor β.[23]

Gas solubility and transport in poly(vinyl chloride)

Solubility and transport of various gases in poly(vinyl chloride) (PVC) are examined based on the experimental results obtained by El-Hibri and Paul,[49] who reported the solubility and permeability isotherms at 35°C of different gases, in the pressure range between 0 and 25 bar.

The experimental solubility isotherms of CO_2, Ar, CH_4, and N_2 illustrated in Figure 7 are first analyzed using the NELF model; the density of the pure unpenetrated glassy polymer is retrieved from the original paper by El-Hibri and Paul, while the χ factor is calculated from the pVT data collection by Zoller and Walsh[37]; the corresponding values are reported in Table 3. In the absence of specific equilibrium solubility data, the determination of the binary interaction parameters k_{12} is obtained by the best fit of the experimental solubility data at 35°C; the resulting values are reported in Table 4. As clearly shown in Figure 7, the NELF model accurately describes the experimental solubility data for all the penetrants considered. Interestingly, in the range of pressure investigated, the model predicts zero dilation of the glassy PVC matrix with N_2 and Ar, whereas rather low but nonzero swelling is obtained with more soluble penetrants as CH_4 and CO_2. The very limited solubility of light gases as N_2 and Ar (below 0.2 wt %) is not able to alter appreciably the polymeric matrix, and the system can be considered to be in the limit of infinite solute dilution. Unfortunately, no helium solubility data were included in the original work, and the only information about He solubility in PVC present in the literature is, to the best of our knowledge, the solubility coefficient reported by Tikhomirov et al. at various temperatures.[50] Such values were used to calculate the binary interaction parameter for He/PVC mixtures, equal to $k_{12} = -0.531$ (Table 4).

Figure 8 illustrates the experimental permeability behaviors of the different penetrants reported by El-Hibri and Paul,[49] including also the results of the permeability model calculations. Interestingly, in this case practically horizontal permeability lines are obtained for the different penetrants, and slightly decreasing trends are observed only for CO_2 and CH_4, albeit with a very limited variation (below 10%). This is a direct consequence of the small excess of free volume of PVC, which leads to very small solubilities and approximately constant $\frac{\omega_1}{p_1}$ values.

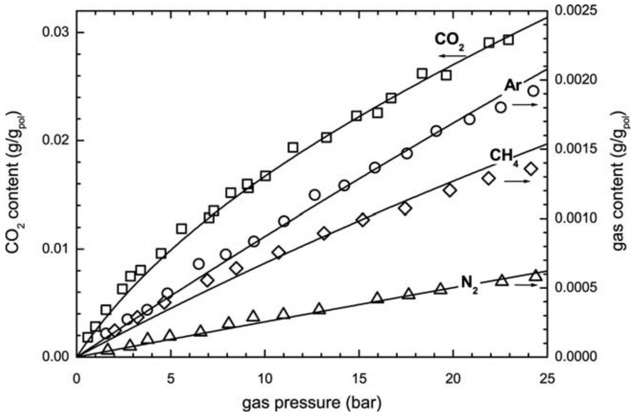

Figure 7. Gas solubility isotherms in glassy poly(vinyl chloride) at 35°C: experimental data after El-Hibri and Paul,[49] together with the NELF model results.

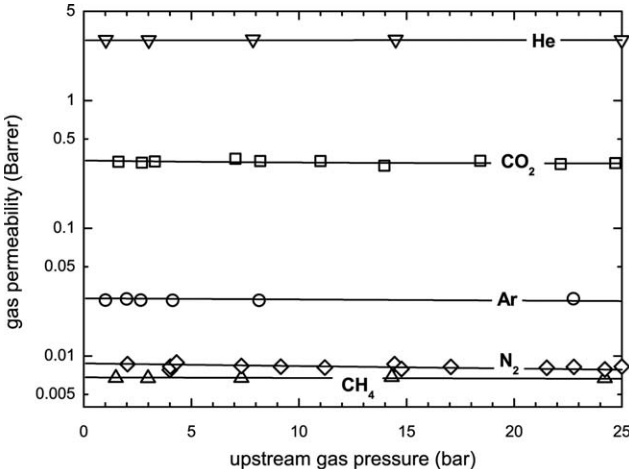

Figure 8. Gas permeability isotherms in glassy poly(vinyl chloride) at 35°C: experimental data after El-Hibri and Paul,[49] together with the transport model results.

The parameters of the transport model here considered are determined from the best fit of the experimental data and, as expected, zero values of plasticization factor β are obtained for all penetrants but CO_2, which is the only gas able to be significantly absorbed in the polymer and consequently to produce appreciable matrix alterations. The resulting parameter values L_{10} and β are reported in Table 5.

Gas solubility and transport in poly(ethylmethacrylate)

The thermodynamic and transport properties in poly(ethylmethacrylate) (PEMA) are investigated with different penetrants, N_2, CH_4, Ar, and CO_2 for proper comparison. The experimental solubility data of N_2, CH_4, and Ar in glassy PEMA, obtained at 35°C by Chiou and Paul,[51] are reported in Figure 9, which also includes the NELF model calculations, as well as CO_2 isotherm. The application of the model is obtained using the pure polymer density indicated in the original paper,[51] and the factor χ calculated in a previous work[34] (Table 3). The binary interaction parameters for the polymer and each penetrant, k_{12}, are obtained from the best fit of the experimental data; the resulting values are reported in Table 4.

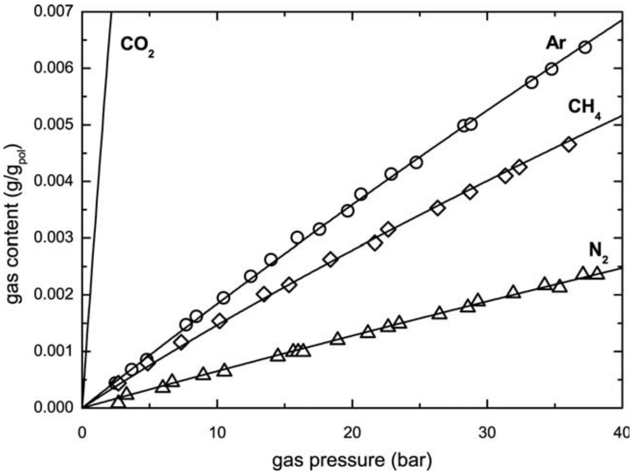

Figure 9. Gas solubility isotherms in glassy poly(ethylmethacrylate) at 35°C: experimental data after Chiou and Paul,[51] together with the NELF model results.

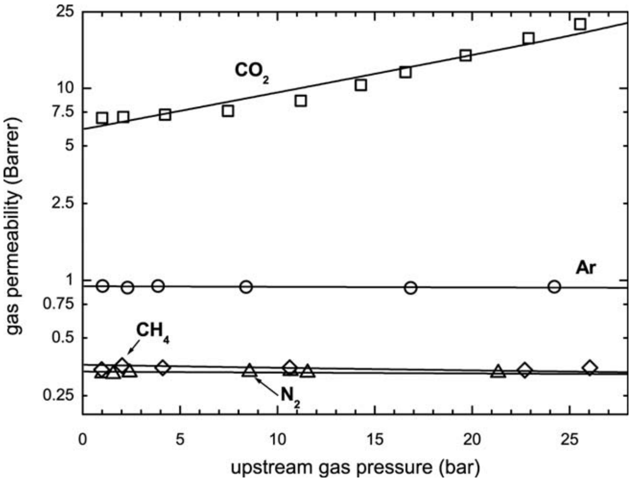

Figure 10. Gas permeability isotherms in glassy poly(ethylmethacrylate) at 35°C: experimental data after Chiou and Paul,[51] together with the transport model results.

Clearly, the model provides a very accurate description of the experimental data in the broad range of pressures considered (Figure 9), which is indeed rather wide (up to 40 bar). Noticeably, the model calculations indicate that a non-negligible swelling is associated to CH_4 and Ar sorption.

The permeability behavior of the same light gases is analyzed through the experimental data reported in the same work,[51] and illustrated in Figure 10 together with the curves obtained by the transport model calculations. Interestingly, in this case, the frequent behavior of gas permeability in glassy polymers, decreasing with increasing upstream penetrant pressures, is not observed: approximately constant values of P_1 are indeed observed for Ar, CH_4, and N_2, whereas a strongly increasing dependence is observed for CO_2 permeability, as already discussed in a previous work.[23] The transport model provides an accurate description of the experimental permeability behavior, and the parameters L_0 and β, obtained from the best fit of the experimental data, are reported in Table 5.

It is noteworthy that not only CO_2, but also Ar and CH_4, seem able to produce a non-negligible effect on the polymer matrix, as suggested by the nonzero values of β. However, the increases in mobility coefficient are always rather limited in view of the small penetrant solubility, always below 1 wt % in the range of pressures inspected. This result is in accordance with the relevant swelling predicted by the NELF model for sorption of Ar and CH_4 in glassy PEMA. Conversely, the rather scarce interaction of N_2 with PEMA and its limited uptake even at high pressure do not allow any modification of the polymer matrix. Therefore, both solubility and mobility coefficient do not change with increasing penetrant pressure, thus leading to constant permeability values.

Gas solubility and transport in poly(phenylene oxide)

Finally, the permeation in poly(phenylene oxide) (PPO) is inspected considering the experimental data reported by Toi et al.[12] The solubility isotherms of Ar, CH_4, and N_2 at 35°C in glassy PPO are illustrated in Figure 11, which includes

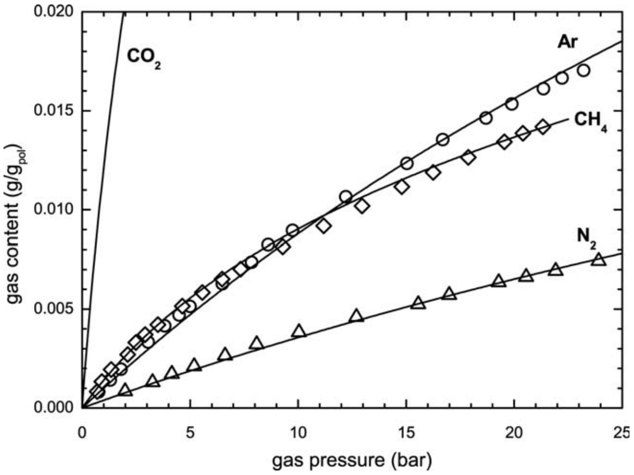

Figure 11. Gas solubility isotherms in glassy poly(phenylene oxide) at 35°C: experimental data after Toi et al.,[12] together with the NELF model results.

also the curves obtained by the NELF model calculations. The results of CO_2 uptake are also reported for the sake of comparison, showing the remarkable difference between CO_2 and light gases uptake.

Also in the present case, the experimental behavior is accurately represented by the NELF model; the resulting values of the binary parameters k_{12}, obtained from the best fit of the data in the whole pressure range, are reported in Table 4.

The description of the thermodynamic behavior of these light gases in glassy PPO allows the application of the transport model considered to calculate the permeability isotherms of the different penetrants. Figure 12 compares the experimental data by Toi et al.[12] with the permeability results obtained by the model calculations, for Ar, CH_4, N_2, and CO_2. The permeability of all gases decreases with increasing upstream pressure, as is most frequent for glassy polymers.

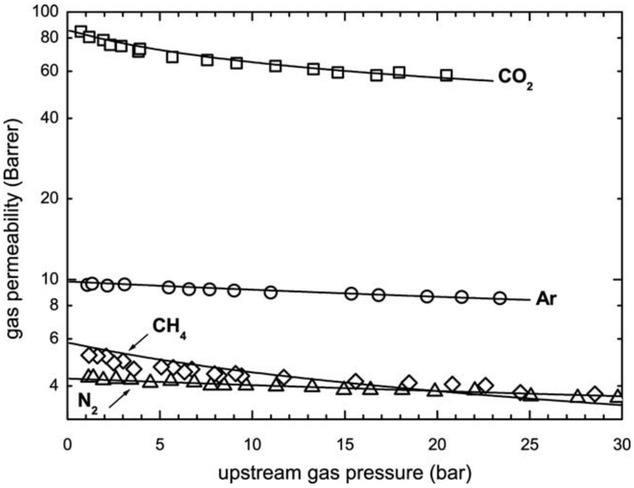

Figure 12. Gas permeability isotherms in glassy poly(phenylene oxide) at 35°C: experimental data after Toi et al.,[12] together with the transport model results.

Table 6. Critical Volumes of the Different Penetrants Investigated[52]

	V_c (cm^3/mol)
He	57.5
Ar	75.0
N_2	89.3
CO_2	91.9
CH_4	98.6
C_2H_4	131.1

The values of the mobility parameters L_{10} and β, retrieved from the analysis of the experimental data, are reported in Table 5, and show a zero plasticization factor for N_2, which is not inducing any modification of the polymer matrix, as well as no polymer swelling, as also confirmed by the NELF model. Conversely, besides the case of CO_2 already discussed in a previous work,[23] increasing values of mobility coefficient with penetrant content in PPO are obtained for Ar and CH_4, resulting in a nonzero plasticization factor β, equal to 3 and 8, respectively. However, due to its rather limited solubility, the mobility coefficient of Ar in PPO shows only very minor changes with concentration, from 1.2×10^{-7} to 1.3×10^{-7} cm^2/s, and the plasticization effect is thus very limited. More significant enhancement of mobility coefficient is obtained for CH_4, whose β factor has intermediate values between those of Ar and CO_2; consequently, increasing values of mobility from 1.9×10^{-8} to 2.2×10^{-8} cm^2/s are obtained in the range of pressure investigated.

Clearly, our model is able to provide very good descriptions of the experimental trend, with average errors below 5%, which are in the same order of typical experimental errors in permeation tests. As the parameters L_{10} and β were obtained from the analysis of experimental permeability data, it is of interest to inspect how errors in their determination affect the value calculated for permeability.[24] Errors in the determination of the infinite dilution mobility propagate linearly into the deviations in the final permeability values. Conversely, for those cases in which non-negligible plasticization is observed (mainly for CO_2 and C_2H_4, but also for CH_4 and Ar to a lesser extent), errors in the plasticization factor β have in general a nonlinear effect on the resulting

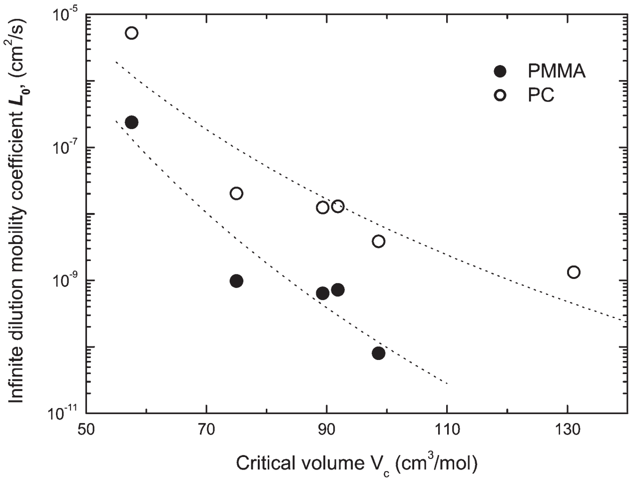

Figure 13. Correlation of infinite dilution mobility coefficient L_{10} in PMMA and PC, with penetrant critical volume.

Table 7. Fractional Free Volume (FFV) Values for the Different Glassy Polymers Considered[24]

	FFV
PMMA	0.116
PC	0.152
PPO	0.177
PSf	0.142
PVC	0.125
PEMA	0.151

permeability. However, when the penetrant content in the polymer matrix is rather low, as is the case of light gases, the error on β produces small deviation in the resulting permeability, while much larger error on P_1 are produced as the gas concentration increases. More specifically, a $\pm 1\%$ error on L_{10} results in a $\pm 1\%$ error in P_1, while a $\pm 1\%$ error in β results in a smaller or higher error on P_1 if $\beta\omega_1 > 1$ or if $\beta\omega_1 < 1$, respectively.

Model parameter correlations

The analysis performed on the permeability of light gas in various glassy polymers led to mobility parameter values that describe the experimental permeability behaviors (Table 5), accounting also for the cases in which mobility L_1 is increasing with penetrant concentration, which require nonzero values of the plasticization factor β.

It is now interesting to inspect what correlations, if any, hold true between the two main parameters, pre-exponential factor, L_{10}, and plasticization factor, β, and the relevant physical properties of both penetrant and polymer. It has been shown that in a single polymer the infinite dilution mobility coefficient L_{10} is strictly related to the size of the probe molecule, represented by penetrant critical volume or kinetic diameter.[26] Conversely, significant differences are observed for the values of L_1 of the same penetrant in various polymers, mainly depending on the excess free volume of the matrix, estimated, for example, by the fractional free volume FFV.[24]

The plasticization factor, in turn, accounts for the enhancement in mobility of the penetrating molecules due to the presence of the penetrant absorbed in the polymer matrix. For this reason, the values of β can be well correlated to the polymer swelling induced by the solutes, which can be accurately described in a quantitative manner through the NELF model analysis of solubility isotherm.[24,26] However, the light gases, such as N_2, He, or Ar considered in the present work, induce very limited or even negligible plasticization in the polymer matrix, in view of their very small solubility, so that no appreciable value of β is actually applicable; consequently, no correlation for β is in order.

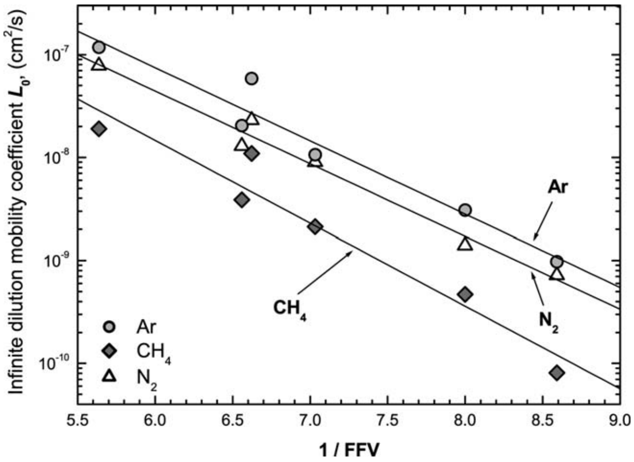

Figure 14. Correlation of infinite dilution mobility coefficient L_{10} with polymer free volume FFV, for the different penetrants.

The mobility coefficients L_1, obtained by the analysis performed on all experimental permeability data examined (Table 5) show a broad range of values, spanning over five orders of magnitude, as very different penetrant and polymer systems are considered. Small penetrant molecules as helium are characterized by the highest mobility, while much lower values are obtained for larger probes, such as methane or ethylene, as expected intuitively and also on the basis of the correlation recalled above. Table 6 reports the values of critical volume of the different penetrants here considered, for clarity sake.

Figure 13 reports the infinite dilution mobility coefficients for the different penetrants, showing a clear monotonous decrease as penetrant critical volume increases. Only the cases of PC and PMMA are presented in Figure 13, and the values obtained for the other polymers are omitted to improve the readability of the chart. The same qualitative behavior is also observed for all the other polymers inspected, as is also apparent from the data reported in Table 5. PC and PMMA are selected as they are characterized by rather different excess free volume, resulting in more than one order of magnitude difference in the mobility coefficients.

The mobility coefficients calculated for each gas in different polymers span over 2–3 orders of magnitude, from the lowest value in PMMA to the highest in PPO, among the polymers here analyzed. In fact, the mobility coefficient depends significantly on the polymer free volume, available to the penetrant molecule to diffuse, as it was already observed for the case of CO_2.[24] The fractional free volume, FFV, is often used to that aim, following the common approach indicated by Bondi[53]

$$\mathrm{FFV} = \frac{\hat{V}_2 - \hat{V}_2^0}{\hat{V}_2} = 1 - \rho_2 \left(1.3\ \hat{V}_2^{\mathrm{VdW}}\right) \tag{10}$$

in which the volume occupied by the polymer macromolecules is calculated from the van der Waals volume, $\hat{V}_2^{\mathrm{VdW}}$. For the polymers here considered, the FFV values used were calculated in a previous work[24] and are reported in Table 7.

Figure 14 reports the resulting L_{10} values for Ar, N_2, and CH_4 as function of the polymer FFV, similarly to what was already discussed for the mobility of CO_2.[24]

Clearly, the mobility coefficient scales exponentially with the reciprocal FFV, and the strong correlation is apparent for all the light gases considered; the three curves are well separated from one another as a consequence of the different penetrant size.

Conclusions

The permeabilities of low molecular weight species, He, Ar, N_2, and CH_4, in various glassy polymers have been analyzed by means of the thermodynamic approach recently proposed by Minelli and Sarti.[23] The model describes the penetrant diffusivity in polymer phases as the product of the mobility L_1, a purely kinetic parameter, and a thermodynamic factor α, related to the dependence of chemical potential on the concentration of the diffusant. The latter factor is readily calculated for glassy polymers by the NELF model, which in turn provides also, at all pressures, the appropriate penetrant solubility coefficient required for the calculation of permeability. It has been shown that the simple expression developed is able to describe accurately the permeability behaviors of different gases in various polymer systems, accounting for the various different types of behaviors observed as upstream pressure increases, namely constant or decreasing or also increasing with penetrant pressure. Most of the experimental curves have been described by means of a single adjustable parameter, the mobility coefficient, which is assumed to remain constant at all concentrations for the light gases considered, in view of their small solubility. Only in some specific cases, an exponential dependence on penetrant concentration is necessary to account for a certain softening or plasticization occurring in the polymer matrix.

The values of L_1 obtained by the model analysis show that the mobility is significantly affected by the penetrant size, and the larger is the molecular size the smaller is mobility, following a clear correlation with penetrant critical volume. Conversely, the infinite dilution mobility coefficient of each penetrants considered correlates well with the polymer fractional free volume, FFV, similarly to what was already found for CO_2.[24]

Literature Cited

1. Baker R. *Membrane Technology and Applications, 3rd ed. Chichester, UK: Wiley, 2012.*
2. Bernardo P, Drioli E, Golemme G. Membrane gas separation: a review/state of the art. *Ind Eng Chem Res*. 2009;48:4638–4663.
3. Scholes CA, Stevens GW, Kentish SE. Membrane gas separation applications in natural gas processing. *Fuel*. 2012;96:15–28.
4. Lange J, Wyser Y. Recent innovations in barrier technologies for plastic packaging – a review. *Packag Technol Sci*. 2003;16:149–158.
5. Masi P, Paul DR. Modeling gas transport in packaging applications. *J Membr Sci*. 1982;12:137–151.
6. Vieth WR, Sladek KJ. A model for diffusion in a glassy polymer. *J Colloid Sci*. 1965;20:1014–1033.
7. Paul DR. Effect of immobilizing adsorption on the diffusion time lag. *J Polym Sci Part A-2: Polym Phys*. 1969;7:1811–1818.
8. Paul DR, Koros WJ. Effect of partially immobilizing sorption of permeability and the diffusion time lag. *J Polym Sci Polym Phys Ed*. 1976;14:675–685.
9. Koros WJ, Paul DR, Rocha AA. Carbon dioxide sorption and transport in polycarbonate. *J Polym Sci Polym Phys Ed*. 1976;14:687–702.
10. Barbari TA, Koros WJ, Paul DR. Gas sorption in polymers based on bisphenol-A. J *Polym Sci Part B: Polym Phys*. 1988;26:729–744.
11. Barbari TA, Koros WJ, Paul DR. Gas transport in polymers based on bisphenol-A. J *Polym Sci Part B: Polym Phys*. 1988;26:709–727.
12. Toi K, Morel G, Paul DR. Gas sorption and transport in poly(phenylene oxide) and comparisons with other glassy polymers. *J Appl Polym Sci*. 1982;27:2997–3005.
13. Stern SA, Saxena V. Concentration-dependent transport of gases and vapors in glassy polymers. *J Membr Sci*. 1980;7:47–59.
14. Zhou S, Stern SA. The effect of plasticization on the transport of gases in and through glassy polymers. *J Polym Sci Part B: Polym Phys*. 1989;27:205–222.
15. Doghieri F, Biavati D, Sarti GC. Solubility and diffusivity of ethanol in PTMSP: effects of activity and of polymer aging. *Ind Eng Chem Res*. 1996;35:2420–2430.
16. Minelli M, Cocchi G, Ansaloni L, Giacinti Baschetti M, De Angelis MG, Doghieri F. Vapor and liquid sorption in matrimid polyimide: experimental characterization and modeling. *Ind Eng Chem Res*. 2013;52:8936–8945.
17. Wang L, Corriou JP, Castel C, Favre E. Transport of gases in glassy polymers under transient conditions: limit-behavior investigations of dual-mode sorption theory. *Ind Eng Chem Res*. 2013;52:1089–1101.
18. Petropoulos JH. On the dual mode gas transport model for glassy polymers. *J Polym Sci Part B: Polym Phys*. 1988;26:1009–1020.
19. Islam MA, Buschatz H. Gas permeation through a glassy polymer membrane: chemical potential gradient or dual mobility mode? *Chem Eng Sci*. 2002;57:2089–2099.
20. Koros WJ, Madden W. Comments on "gas permeation through a glassy polymer membrane: chemical potential gradient or dual mobility model?" by M.A. Islam and H. Buschatz [Chemical Engineering Science 57 (2002) 2089–2099]. *Chem Eng Sci*. 2003;58: 2461–2463.
21. Barbari TA. Dual-mode free volume model for diffusion of gas molecules in glassy polymers. *J Polym Sci Part B: Polym Phys*. 1997; 35:1737–1746.
22. Lee DK, Kim YW, Lee KJ, Min BR, Kim JH. Thermodynamic model of gas permeability in polymer membranes. *J Polym Sci Part B: Polym Phys*. 2007;45:661–665.
23. Minelli M, Sarti GC. Permeability and diffusivity of CO_2 in glassy polymers with and without plasticization. *J Membr Sci*. 2013;435: 176–185.
24. Minelli M, Sarti GC. Permeability and solubility of carbon dioxide in different glassy polymer systems with and without plasticization. *J Membr Sci*. 2013;444:429–439.
25. Minelli M, Doghieri F. Thermodynamic basis for vapor solubility in ethyl cellulose. *J Membr Sci*. 2014;469:336–343.
26. Minelli M, Sarti GC. Thermodynamic basis for vapor permeability in ethyl cellulose. *J Membr Sci*. 2015;473:137–145.
27. Minelli M. Modeling CO_2 solubility and transport in poly(ethylene terephthalate) above and below the glass transition. *J Membr Sci*. 2014;451:305–311.
28. Doghieri F, Sarti GC. Nonequilibrium lattice fluids: a predictive model for the solubility in glassy polymers. *Macromolecules*. 1996; 29:7885–7896.
29. De Angelis MG, Sarti GC. Solubility of gases and liquids in glassy polymers. *Annu Rev Chem Biomol Eng*. 2011;2:97–120.
30. Doghieri F, Sarti GC. Predicting the low pressure solubility of gases and vapors in glassy polymers by the NELF model. *J Membr Sci*. 1998;147:73–86.
31. Sarti GC, Doghieri F. Predictions of the solubility of gases in glassy polymers based on the NELF model. *Chem Eng Sci*. 1998;53:3435–3447.
32. Lacombe RH, Sanchez IC. Statistical thermodynamics of fluid mixtures. *J Phys Chem*. 1976;80:2568–2580.
33. Sanchez IC, Lacombe RH. Statistical thermodynamics of polymer solutions. *Macromolecules*. 1978;11:1145–1156.
34. Minelli M, Doghieri F. A predictive model for vapor solubility and volume dilation in glassy polymers. *Ind Eng Chem Res*. 2012;51: 16505–16516.
35. Vrentas JS, Duda JL. Diffusion in polymer-solvent systems. I. Reexamination of the free-volume theory. *J Polym Sci Polym Phys Ed*. 1977;15:403–416.
36. De Angelis MG, Sarti GC, Doghieri F. NELF model prediction of the infinite dilution gas solubility in glassy polymers. *J Membr Sci*. 2007;289:106–122.
37. Zoller P, Walsh DA. *Standard Pressure–Volume–Temperature Data for Polymers. Lancaster, PA: Technomic, 1995.*
38. Rodgers P. Pressure–volume–temperature relationships for polymeric liquids: a review of equations of state and their characteristic parameters for 56 polymers. *J Appl Polym Sci*. 1993;48:1061–1080.
39. Minelli M, Doghieri F. Predictive model for gas and vapor solubility and swelling in glassy polymers I: application to different polymer/penetrant systems. *Fluid Phase Equilib*. 2014;381:1–11.
40. Koros WJ, Chan AH, Paul DR. Sorption and transport of various gases in polycarbonate. *J Membr Sci*. 1977;2:165–190.
41. Jordan SS, Koros WJ. A free volume distribution model of gas sorption and dilation in glassy polymers. *Macromolecules*. 1995;28: 2228–2235.
42. Erb AJ, Paul DR. Gas sorption and transport in polysulfone. *J Membr Sci*. 1981;8:11–22.
43. Smith ZP, Tiwari RR, Dose ME, Gleason KL, Murphy TM, Sanders DF, Gunawan G, Robeson LM, Paul DR, Freeman BD. Influence of diffusivity and sorption on helium and hydrogen separations in hydrocarbon, silicon, and fluorocarbon-based polymers. *Macromolecules*. 2014;47:3170–3184.

44. Udel P-3500 Technical Data Sheet. Available at http://catalog.ides.com/Datasheet.aspx?I=92041&U=0&FMT=PDF&E=73899.
45. Chiou JS, Paul DR. Sorption and transport of inert gases in PVF_2/PMMA blends. *J Appl Polym Sci*. 1986;32:4793–4814.
46. Chiou JS, Paul DR. Sorption and transport of CO_2 in PVF_2/PMMA blends. *J Appl Polym Sci*. 1986;32:2897–2918.
47. Durill PL, Griskey RG. Diffusion and solution of gases in thermally softened or molten polymers: part I. Development of technique and determination of data. *AIChE J*. 1966;12:1147–1151.
48. Matteucci S, Yampolskii Y, Freeman BD, Pinnau I. Transport of gases and vapors in glassy and rubbery polymers. In: Yampolskii Y, Pinnau I, Freeman BD, editors. *Materials Science of Membranes for Gas and Vapor Separation. New York: Wiley, 2006:1–47.*
49. El-Hibri MJ, Paul DR. Effects of uniaxial drawing and heat-treatment on gas sorption and transport in PVC. *J Appl Polym Sci*. 1985;30:3649–3678.
50. Tikhomirov BP, Hopfenberg HB, Stannett V, William JL. Permeation, diffusion, and solution of gases and water vapor in unplasticized poly(vinylchloride). *Makromol Chem*. 1968;118:177–188.
51. Chiou JS, Paul DR. Gas sorption and permeation in poly(ethyl methacrylate). *J Membr Sci*. 1989;45:167–189.
52. NIST Standard Reference Database. Available at www.NIST.gov.
53. Bondi A. *Physical Properties of Molecular Crystals, Liquids and Glasses. New York: Wiley, 1968.*

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