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Modeling Sorption Kinetics of Carbon Dioxide in Glassy Polymeric Films Using the Nonequilibrium Thermodynamics Approach

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The nonequilibrium thermodynamics of glassy polymers (NET-GP) approach (*Macromolecules* 2005, *38*, 10299.) has been applied to the development of a one-dimensional transport model aimed at describing the kinetics of sorption and dilation of polymeric films in supercritical carbon dioxide. The NET-GP model was combined with a simple rheological constitutive equation to build a sorption–diffusion–relaxation model able to describe mass uptake and swelling kinetics of polymeric films in contact with carbon dioxide over a wide range of pressures and temperatures. The model calculations are compared with data on mass sorption kinetics for CO_2 in supported glassy poly(methyl methacrylate) (PMMA) films, measured in a high-pressure quartz crystal microbalance (QCM).

Introduction

Carbon dioxide is gaining interest as a solvent for industrial applications because of its unique characteristics, such as nonflammability, low toxicity, natural abundance, low cost, and environmental compatibility.[1,2] At supercritical conditions, CO_2 has a gaslike viscosity, a low surface energy and a liquidlike density, allowing it to penetrate into small surface features and exhibit enhanced solubility and transport properties. In addition, the solvent power of CO_2 can be easily tuned by small changes in temperature and pressure.

As a result, there is a wide range of applications in which CO_2 could replace traditional aqueous and organic solvents, from the food industry, to coatings in the automotive and furniture industries, to polymer production and processing.[3] Of particular interest is the ability of CO_2 to swell and plasticize many polymers, which makes it ideal for the manipulation of polymer physical properties to enhance the diffusion of small molecules or for use as a foaming agent.[4,5]

Modeling the transport of solvents in glassy polymeric materials is of paramount importance in controlling numerous processes such as drug impregnation and release, membrane separations, photolithography, and fabrication of microelectronic devices. These transport models could eventually allow for process optimization and would facilitate the extension of known results to different systems or applications. On the other hand, the mathematical description of the sorption of swelling agents in glassy polymers is a difficult task in view of the changes in structure of the polymeric materials induced by the diffusion of penetrant molecules. Indeed, several different types of transport behavior have been observed experimentally over the years for various polymer–penetrant pairs at different operating conditions.[6–11] In general terms, it can be said that the penetration of swelling agents into polymeric films enhances the free volume of the system and the mobility of the polymer chains, lowering the glass transition temperature and allowing the matrix to relax.[12] In turn, these factors strongly affect the additional adsorption and diffusion of penetrant molecules.

The aim of the present work is to introduce a new sorption–diffusion–relaxation model for studying the mass uptake and swelling kinetics of polymeric films brought into contact with swelling agents such as CO_2. It is a direct application and enhancement of the nonequilibrium thermodynamics of glassy polymers (NET-GP) approach, initially introduced by Doghieri and Sarti [13,14] for the study of sorption in glassy polymers at low pressures and recently extended by Carlà et al.[15] to high-pressure regions.

The NET-GP approach can be used to extend the applicability of any suitable equilibrium model for the free energy of a polymer–solute mixture in the rubbery region over into the nonequilibrium glassy region, by means of the use of the polymer density as an order parameter that describes the degree to which the system is away from its equilibrium state. From this perspective, the order parameter is considered to be a function not only of thermodynamic variables, such as temperature, pressure, and composition, but also of the thermal, mechanical, and sorption history of the sample. In previous studies,[15] the pseudoequilibrium polymer density below the glass transition point was estimated by means of a linear dependence on the gas pressure. Although this approach was sufficient for calculating the sorption isotherms, an evolution equation for the polymer density is necessary to describe the kinetics of the relaxation process under experimental conditions that induce a glass–rubber transition in the polymer.

Although a review of modeling efforts to represent the coupling between diffusion and relaxation in glassy polymers is beyond the aim of this work, it is useful to remember that the concept of polymer relaxation induced by the stress exerted by the diffusion of swelling agents dates back to the early work of Newns.[16] Several attempts followed in describing the driving force for the relaxation process in polymer–solute mixtures, relying on different functional forms for the analysis of the mechanical response of the glassy polymeric materials to the swelling stress. Sarti[17] used the difference in the chemical potential between the pure polymer and the swollen polymer as the driving force for polymer swelling. Sarti and Apicella revised this approach by considering the nonequilibrium state of the glassy polymer, adding an excess term to the equilibrium driving force.[18] A similar expression for the chemical potential

was used by Bisschops et al.,[19] and its gradient was used as the driving force for swelling.

The present work introduces a model that is able to represent quantitatively the coupling between diffusion and swelling through a consistent, although simplified, thermodynamic approach. The driving force for the relaxation processes is directly derived from the thermodynamic development of the NET-GP model and does not require a separate assumption. Following the basic idea that the out-of-equilibrium degree of the glassy matrix is properly described by the volume deformation of the polymer network, an evolution equation for the corresponding order parameter is obtained in which an expression for the stress induced by the swelling agents emerges in a straightforward manner.

Well-established general relations can then be used for the solute diffusive flux, expressed in a form that is consistent with the representation chosen for the thermodynamic properties. No specific effort has been made here to relate transport properties such as the diffusion coefficient or the bulk viscosity of the polymer to the thermodynamic state of the system. Indeed, whereas several reliable expressions for such properties are available for temperatures above T_g, the development of useful representations of the same variables below T_g is still an unresolved problem. Useful correlations and interpretative models for mass diffusivity[10,11,20] and viscosity[22] in polymer−penetrant systems as functions of temperature, pressure, and solute concentration in the rubbery state have been introduced in the literature and compared extensively with experimental results. The complexities of the behavior of glassy polymer−penetrant systems below T_g have not, as yet, allowed for the development of correlations of diffusion coefficient and rheological properties under these conditions, and the interesting models proposed so far for these variables have not yet been compared extensively with experimental data.[23] The model derived in this work is compared to sorption experiments in which the volume deformation of the polymer network and the solute content do not vary greatly during a single experimental run. These sorption experiments were done using a jump from a lower pressure to a higher pressure. As a result, the analysis of the measured sorption data was performed assuming constant values for transport properties within the same sorption run. The solute diffusivity and bulk viscosity were treated as adjustable parameters in the analysis of the data, and their resulting variations with average solute concentration during the pertinent sorption step are discussed.

Kinetic sorption data analyzed in this work are part of an extensive study on the CO_2−poly(methyl methacrylate) (PMMA) system, and the equilibrium and pseudoequilibrium solubility and swelling were presented in a previous work.[15] In this article, a discussion of the kinetics of sorption runs below the glass transition temperature is presented. A brief description of the apparatus used for the sorption experiments with high-pressure CO_2 in supported PMMA films is also provided. The model used for the interpretation of sorption kinetic data during pressure-jump experiments is then presented in detail. The relation of the proposed kinetic model to the thermodynamic framework of the NET-GP approach is specifically addressed. A comparison of experimental data for CO_2 sorption in glassy PMMA with the results of the kinetic model is analyzed in view of the possible uses of the latter in describing general sorption problems in glassy polymer systems.

Experimental Section

A high-pressure quartz crystal microbalance (QCM) apparatus was used to perform sequences of differential sorption experiments for CO_2 in supported PMMA films. After an apparent equilibrium had been reached for a film exposed to a CO_2 atmosphere at an initial pressure of P^{in}, a step increase in CO_2 pressure was imposed to a final pressure of P^{fin}, and the resulting mass uptake in the PMMA film was monitored as a function of elapsed time for a few hours until a new apparent equilibrium for the solute content in the polymeric film was reached. Several differential pressure jump steps were realized by increasing the CO_2 pressure to 120 bar at 50 °C under supercritical conditions for the pure solute gaseous phase.

Materials. Coleman-grade (purity > 99.999%) CO_2 was obtained from National Welders. Poly(methyl methacrylate) having a molecular weight of 72 kDa and a polydispersity index (PDI) of 1.08 was obtained from Polymer Source Inc. (Montreal, Canada). A 5 wt % PMMA solution in toluene (Fisher) was used for film preparation by dip coating. All materials were used as received.

Dilation Measurements. A high-precision microbalance was used to evaluate the mass density of the dry polymer samples, and film dilation under sorption conditions were measured by means of a high-pressure ellipsometer. Details about the apparatuses and procedures used to measure the volume dilation of polymeric films are available elsewhere.[15]

QCM System. The quartz crystals used in this study, obtained from International Crystal Manufacturing and used as received, were 5.00 MHz AT-cut Si with a blank diameter of 8.5 mm and a thickness of 0.25 mm. The root-mean-square surface roughness of the crystals used was less than 10 nm [analyzed by atomic force microscopy (AFM)]. A voltage-controlled oscillator was used (Maxtek model PLO-10) to provide both frequency and voltage outputs. The voltage reading is inversely proportional to the resistance of the crystal. An Agilent 225 MHz Universal Frequency Counter (model 53131A) was used to monitor the frequency.

Pressure Cell Apparatus. The custom-built pressure cell consisted of a thick-wall cylinder (63.5 mm i.d. × 200 mm height), with a high-pressure electrical feedthrough for QCM connections. A high-pressure thermocouple (Omega) was used to measure the cell temperature, and a pressure transducer (Omega, part No. PX 302) was used to monitor the pressure. The whole assembly was placed in a water bath, and its temperature was controlled to within ±0.1 °C. All data acquisition for frequency, voltage, temperature, and pressure was carried out using LabView.[15]

Polymer Film Preparation. After the fundamental frequency of the clean crystal in vacuum, F_o, had been measured, the crystal was dipped vertically into the PMMA solution in toluene for 1 min and withdrawn from the solution at a controlled rate. The coated crystal was then dried under vacuum at 76 °C for approximately 1 h. The frequency was measured after the sample had been dried; a constant stable frequency level was an indication of sufficient solvent removal. The value of the stabilized frequency of the coated QCM in vacuum was used to calculate the initial total mass of coated polymer, and this mass was, in turn, used with the bulk polymer density[15] to estimate the film thickness. Relatively small variations in film thickness were measured in different experimental runs, ranging from 1.0 to 1.1 μm. Cross-sectional SEM images of the coated QCM crystals support this estimation. The film roughness, as measured by AFM for samples before and after treatment with CO_2, was about 5 nm.

Sorption Experiments. After a stable signal had been achieved in vacuum, the pressure was increased stepwise. The frequency was then allowed to reach the new stable level. The
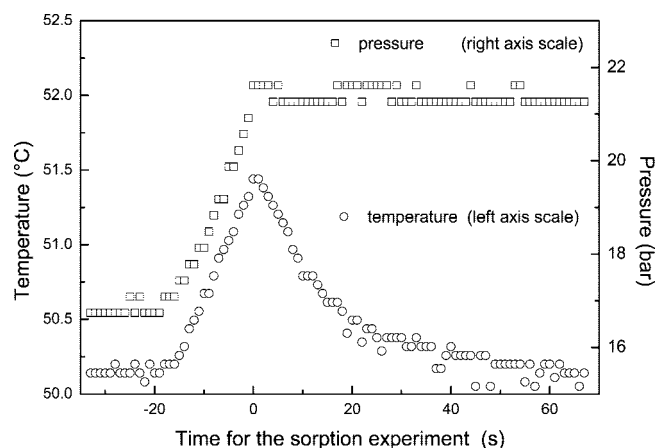
Figure 1. Example of kinetics for cell pressure and temperature at early stages in a sorption step.

same procedure was then used for subsequent steps. Results for mass uptake at pseudoequilibrium in differential sorption steps were consistently reproducible, as shown by results measured in separate sequences of differential sorption steps.

Nonisothermal Conditions. For the following discussion, it is relevant to note that, although all possible efforts were made to achieve isothermal stepwise pressure increases to start any sorption step, an increase in cell temperature as a result of gas inlet could not be avoided. An example of data recorded for gas-phase temperature and pressure is given in Figure 1 as a function of time in a sorption step. A peak in cell temperature can be observed from measurements, with the maximum corresponding to the time at which the final pressure for the step is reached (e.g., see in Figure 1 the measured temperature and pressure data for one example of a start procedure in a sorption step experiment). At the early stages of sorption, the gas temperature decreases according to a rate that depends on the heat capacity, surface area, and heat-transfer coefficient in the gas phase. Although limited in magnitude and duration, deviations from isothermal conditions can affect the results for sorption kinetics in the experiments of interest here, in view of the highly exothermic character of gas sorption in glassy polymers and the remarkably small value for the characteristic time of the diffusion process. Attempts to account for deviations from isothermal conditions considered in this work are presented in the subsequent sections.

Theory

This section describes the formulation of the isothermal and isobaric mass-transport model considered in this work, aimed at a description of mass sorption in supported polymeric films induced by a sudden increase in the solute fugacity imposed at the external boundary. The model introduced here, which specifically addresses the case of a swelling agent, is framed within the NET-GP thermodynamic model and stresses the role of sorption-induced volume relaxation phenomena in the polymeric system. In turn, it neglects the effects of noninstantaneous heat transfer or complex mechanical constraints in the sample, which could ultimately result in nonuniform and/or transient temperature and pressure fields, respectively, in the polymer. Field equations are presented here in one-dimensional form, as is consistent with the experimental case of transport in supported films with negligible border effects.

Evolution Equation for the Polymer Density. According to a key assumption in the NET-GP approach, the polymer
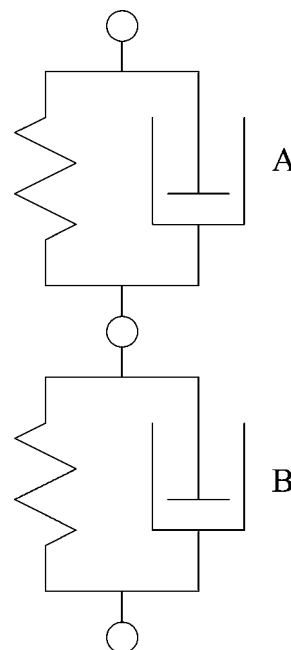

Figure 2. Mechanical representation of a two-Voigt-element rheological model.

density is treated as an order parameter that specifies the degree to which the system is out of equilibrium. Although the volume deformation behavior of polymeric species below the glass transition temperature can be extremely complex when considered in general terms,[24] only the relatively simple problem of representing the process of volume dilation of the glassy polymer during the time scale of a sorption experiment is of interest here.

With this aim, a simple model, whose mechanical equivalent is represented by a system of two Voigt elements arranged in series (see Figure 2), is used to derive a constitutive equation for the volume deformation in the polymeric mixture. According to this assumption, the total volume per unit mass of polymer, V_p, in the system results from the sum of two contributions, one from each of the two Voigt elements A and B, distributed by a convenient weighting factor χ

$$V_p = \chi V_p^A + (1 - \chi) V_p^B \tag{1}$$

In a general Voigt element, the driving stress for the deformation results from the sum of an elastic term and a viscous term; the former is a direct function of the current value of the deformation, whereas the latter is assumed to be proportional to the deformation rate through a viscosity coefficient. The Voigt model is indeed the simplest approach to describe linear viscoelastic mechanical behavior in creep experiments. For the case of interest here, the deformation is represented by the volume per unit polymer mass in the system, and the driving stress is the effective pressure P. The pure elastic contribution to the stress at a given deformation can be evaluated from the corresponding equilibrium value in the system, $P^{eq}(T,V_p)$. Thus, according to the above assumption, the volumes per unit polymer mass pertinent to each of the two Voigt elements, V_p^A and V_p^B, can be calculated using the evolution equations

$$\frac{1}{V_p^A} \frac{dV_p^A}{dt} = \frac{P^{eq}(T, V_p^A, \mu_s) - P}{\eta^A} \tag{2}$$

and

$$\frac{1}{V_p^B}\frac{dV_p^B}{dt} = \frac{P^{eq}(T, V_p^B, \mu_s) - P}{\eta^B} \quad (3)$$

where P is the system pressure and $P^{eq}(T,V_p,\mu_s)$ is the equilibrium pressure of the polymeric system at the assigned temperature T, chemical potential of solute species μ_s, and volume per unit polymer mass V_p. The viscous contribution to the stress is taken into account through the product of a bulk viscosity, η, and the polymer deformation rate, $(d \ln V_p)/dt$, where the time derivative represents a material derivative for the polymeric species.

It should be observed that, for the case of supported films that are swelling, normal stresses along the in-plane directions are different from those exerted in the out-of-plane directions, and different choices are possible to express the effective pressure P in the polymer phase appearing in eqs 2 and 3. In what follows, it is assumed that the effective pressure P is equal to the normal stress in the out-of-plane direction, and as a result of this assumption, P has the same value at all points along the sample thickness, it is constant in time during an experiment done at constant pressure, and it is equal to the pressure set in the external fluid phase.

In the simplified picture of the polymer rheology considered here, Voigt element A is aimed to describe relatively short-time relaxation phenomena, and the long-time evolution of the system volume is meant to be represented by Voigt element B. Consistent with the physical picture sketched above, the following assumptions are made for the characteristic viscosities of Voigt elements A and B

$$\eta^A = \begin{cases} \eta^* & T \leq T_{gmix}(\omega_s, P) \\ \to 0 & T > T_{gmix}(\omega_s, P) \end{cases}$$
$$\eta^B = \begin{cases} \to \infty & T \leq T_{gmix}(\omega_s, P) \\ \to 0 & T > T_{gmix}(\omega_s, P) \end{cases} \quad (4)$$

where $T_{gmix}(\omega_s,P)$ is the glass transition temperature of the mixture for an assigned value of the solute mass fraction, ω_s, and the pressure, P. In essence, Voigt element A is chosen to have a finite viscosity below the glass transition temperature, whereas the volume of Voigt element B is chosen to be essentially frozen. Both Voigt elements A and B are assumed to have zero viscosity in the rubbery region above the glass transition temperature. Thus, with respect to the transport process of interest here, they behave as general elastic elements above T_{gmix}.

Because of these choices in the properties of the Voigt elements, we can interpret the pseudoequilibrium conditions at the end of a sorption experiment as the state in which deformation of element A in the Voigt model has reached the equilibrium value for the imposed temperature, pressure, and solute fugacity. The out-of-equilibrium degree of the system at the pseudoequilibrium state is then entirely determined by the nonequilibrium value for the deformation of element B in the same model.

An early version of the evolution equation for the order parameter discussed here was presented in a previous work[21] and applied to the analysis of long-term sorption processes in which diffusion resistances can be neglected. In that case, a linear viscoelastic rheological model with a continuous spectrum of relaxation times was considered. In the present work, the above-discussed simplified rheological model is implemented to analyze sorption processes over a considerably shorter time scale in the simplest possible terms.

Estimation of Parameters in the Relaxation Model. The set of equations described above, coupled with proper initial and boundary conditions, allow for a complete description of the transport problem of interest here, when implemented with a proper expression for thermodynamic and transport properties as functions of field variables in the nonequilibrium state of the system.

The thermodynamic properties of interest are the nonequilibrium solute chemical potential, μ_s, and the equilibrium pressure, P^{EQ}. Within the framework of the NET-GP model, both of these properties are functions of temperature and species mass densities

$$\mu_s^{NE} = \mu_s^{NE}(T, \omega_s, \rho_p) \qquad P^{EQ} = P^{EQ}(T, \mu_s, \rho_p) \quad (5)$$

Proper expressions of the above type can be derived from any convenient equations of state for the equilibrium system whose pure-component and binary parameters are evaluated using specific reliable volumetric and solubility data. In what follows, the two-binary-parameter lattice-fluid model by Sanchez and Lacombe has been used as suitable representation of the thermodynamic properties of the CO_2–PMMA mixture, as was already done in a previous work.[15] The rheological properties involved in the model are the bulk viscosity, η^*, and the weighting factor, χ, in the two-element Voigt model for the polymer–solute system. The parameter η^* ultimately labels the short-term bulk viscosity in the glassy polymeric system, and it is treated as an adjustable parameter in the calculations that follow. The parameter χ represents the mass fraction of the pure glassy polymer associated with the relatively short relaxation times for volume dilation. In accordance with the definition in eq 1, it is easy to recognize that the parameter χ can be estimated as the ratio between the apparent isothermal compressibility in the glassy state for relatively short-time experiments and the equilibrium compressibility as measured under rubbery conditions

$$\chi = \frac{k_g^-}{k_g^+} = \frac{\lim_{T \to T_g^-}[(\partial V_{pol}/\partial P)_T/V_{pol}]}{\lim_{T \to T_g^+}[(\partial V_{pol}/\partial P)_T/V_{pol}]} \quad (6)$$

where k_g^- and k_g^+ are the isothermal compressibilities of glassy and rubbery polymer, respectively, both in the limit of the glass transition temperature. It is worthwhile to stress here that the terms above refer to volume changes after pressure variations measured in constant-temperature experiments. In fact, pertinent data for the glassy state (k_g^-) are not abundant in the technical literature, as isothermal experiments are not part of standard procedures for the characterization of volumetric properties of glassy polymers. The above considerations show a possible path for the evaluation of the model parameter χ by means of data obtained from experiments other than sorption runs. When this is the case, a prediction of volume dilation can be attempted, with the assumption that the parameter χ is independent of solute concentration in the polymeric mixture. Indeed, the constant value of the volume per unit polymer mass for element B in the model described above can be estimated from the relation

$$V_p^B = [V_p^0 - \chi V_{p(T,f_s \to 0)}^{EQ}]/(1 - \chi) = V_p^B \quad (7)$$

where V_p^0 is the pseudoequilibrium volume per unit polymer mass at dry conditions and $V_{p(T,f_s \to 0)}^{EQ}$ is the corresponding thermodynamic equilibrium value. The pseudoequilibrium value, V_p^{PE}, of the volume per unit polymer mass at sorption conditions is then calculated as

$$V_{p(T,f_s)}^{PE} = V_p^0 + \chi\left[V_{p(T,f_s)}^{EQ} - V_{p(T,f_s=0)}^{EQ}\right] \qquad (8)$$

The expression in eq 8 accounts for a pseudoequilibrium polymer volume that is equal to the measured volume V_p^0 in the limit of infinitely dilute polymer–solute mixtures and should be considered for the estimation of the volume per unit polymer mass up to the glass transition solute concentration, corresponding to a pressure P_g and solute fugacity f_{s_g}. Based on general results for gas sorption and dilation in glassy polymers, a linear relation for V_p with solute gas pressure was assumed in a previous work,[15] in order to analyze the solubility isotherm below P_g. The latter condition is also attained in eq 8 as long as the equilibrium thermodynamic model accounts for a constant value of solute partial molar volume and solubility coefficient in the fugacity range from vanishing f_s to the glass transition value f_{s_g}.

Mass Balances and Constitutive Equation for the Solute Mass Flux. The continuity equations for the solvent (mass density ρ_s) and polymer (mass density ρ_p) are the only local balance laws considered in the model. For the case of one-dimensional transport, they take the form

$$\frac{\partial \rho_s}{\partial t} = -\frac{\partial}{\partial x}(\rho_s v_{p_x} + j_{s_x}) \qquad (9)$$

$$\frac{\partial \rho_p}{\partial t} = -\frac{\partial}{\partial x}(\rho_p v_{p_x}) \qquad (10)$$

where x indicates the spatial coordinate measuring distance from the polymer substrate and j_s is the out-of-plane component of the diffusive solute flux vector defined by the expression

$$\underline{j}_s = \rho_s(\underline{v}_s - \underline{v}_p) \qquad (11)$$

Here, $\underline{v}_s$ and $\underline{v}_p$ are the mass velocities of the solvent and polymeric species, respectively. The mass diffusive flux for the mobile species can be calculated using a generalized Fickian constitutive equation suitable for concentrated polymer solutions, where the driving force is the gradient in the chemical potential of the solvent in the polymer

$$\underline{j}_s = -\rho_s D_s \underline{\nabla}(\mu_s/RT) \qquad (12)$$

The quantity D_s is a generalized thermodynamic diffusion coefficient for the transport of the solute species in the polymer matrix.

The solvent chemical potential in eq 12 can be determined using the NET-GP approach, which provides an expression for the solvent chemical potential under nonequilibrium conditions

$$\mu_s^{NE} = \mu_s^{NE}(T, \omega_s, \rho_p) \qquad (13)$$

The expression for the nonequilibrium chemical potential is obtained here through use of the NET-GP approach. This theoretical framework is used to carry out a rigorous extension of well-established expressions for the equilibrium free energy of fluid systems to nonequilibrium conditions, by assuming that the polymer density ρ_p is not directly dependent on temperature, pressure, and solute mass fraction.[13–15] An equation of the type reported in eq 13 can be derived, in which the arguments (T,ω_s,ρ_p) are meant to be independent and not directly related to the pressure P in the system, unlike the case of equilibrium models. In view of the assumptions in eqs 12 and 13, regardless of the specific form of the equation used for the free energy, a valid expression for the diffusive mass flux of the solute at constant temperature results in the following terms

$$j_{s_x} = -\rho_s \frac{\partial(\mu_s/RT)}{\partial \omega_s} D_s \frac{\partial \omega_s}{\partial x} - \rho_s \frac{\partial(\mu_s/RT)}{\partial \rho_p} D_s \frac{\partial \rho_p}{\partial x} \qquad (14)$$

Initial and Boundary Conditions. For the case of a differential step change in sorption pressure, from P^{in} to P^{fin}, the initial conditions are written assuming a uniform thermodynamic state for the system throughout the film thickness, corresponding to a pseudoequilibrium state at temperature T and pressure P^{in}.

The interfacial boundary condition derives directly from the phase equilibrium relations. Finally, at the nonpermeable substrate, the flux is taken equal to zero.

$$\begin{cases} t = 0 & \begin{cases} \mu_s(x) = \mu_s^0(T, P^{in}) \\ V_p^A(x) = V_p^{EQ}[T, P^{in}, \mu_{s(T,P^{in})}^0] \\ V_p^B(x) = V_p^B \end{cases} \forall x \in [0, \delta] \\ x = \delta & \mu_s^{NE}(t) = \mu_s^0(T, P^{fin}) \qquad \forall t > 0 \\ x = 0 & j_{s_x}(t) = 0 \qquad \forall t > 0 \end{cases} \qquad (15)$$

Here, δ indicates the time-dependent thickness of the polymer film, and $\mu_s^0(T,P)$ refers to the chemical potential of the pure solute component in the fluid phase at given temperature and pressure. In the above equations, consistent with the picture given above for the rheological properties, equilibrium conditions are assumed for the initial state of finite-viscosity Voigt element A in Figure 1.

Correction for Nonisothermal Conditions. Describing, in detail, the temperature profile within the polymeric film and its evolution in time would require the introduction of the energy balance law and the use of specific information about properties of the solute–polymer mixture as well as the gas phase to which it is exposed and the quartz crystal to which it adheres. On the other hand, the model representation of all details in the experimental results is not the aim of this work, which is instead focused on a discussion of the reliability of the model for two-stage sorption that was introduced earlier in this section. In fact, toward the aim of representing the nature and magnitude of the effect on the mass sorption kinetics that results from deviations from isothermal conditions for the gas phase, a detailed discussion of the temperature profile in the film is not necessary. Indeed, imposing temperature variations in the polymeric films that resemble those measured in the gas phase is sufficient to appreciate those effects. Corrections for nonisothermal conditions in our model, when introduced, are thus attempted here through the direct introduction of a time-dependent temperature for the polymeric film in the model equations already described. The temperature is assumed to be uniform throughout the film thickness at each time in the process. A simple expression of exponential decay in time for temperature deviations is used, which ultimately leads to the following law for the temperature of the polymeric film

$$T(t) = T_{SP} + \Delta T \exp[-(t/t^*)] \qquad (16)$$

where T_{SP} is the set-point temperature in the experiment, ΔT is the maximum value for the estimated temperature deviation, and t^* is the evaluated characteristic time of the temperature evolution in the system. In the calculations whose results are discussed in the following sections, the maximum temperature deviation and characteristic time were estimated for any of the experiments considered from measured data for the gas-phase temperature. The effect of a time-dependent film temperature on the short-term kinetics of mass sorption as predicted by the above-described model results from the temperature
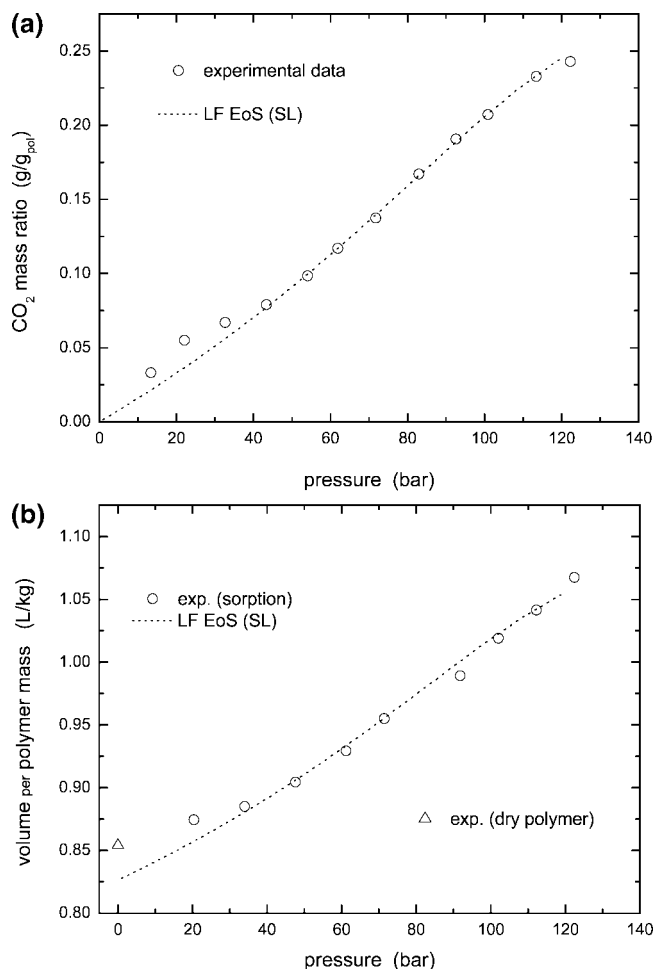
Figure 3. (a) Sorption isotherm and (b) volume-dilation isotherm for the CO_2-PMMA system at 50 °C.

Table 1. Parameters Used in the SL Thermodynamic Model

Pure-Component Parameters		
	CO_2	PMMA
T^* (K)	283	696
P^* (MPa)	659	503
ρ^* (g/cm³)	1.62	1.269
Binary Parameters		
k_{ij}	0.1161	
η_{ij}	−0.015	

sequence of differential sorption experiments are reported in Figure 3b. The data for equilibrium or pseudoequilibrium volume per unit polymer mass as a function of CO_2 pressure in Figure 3b were calculated after the mass density of the dry polymer had been measured in a high-precision laboratory balance and the volume of dilation had been measured in a sorption experiment run on a high-pressure ellipsometer apparatus.[15] The glass transition pressure for the CO_2-PMMA system, as calculated according to different methods, is located somewhere between 40 and 45 bar at 50 °C.[15]

High-pressure (rubber-region) data for both solute content and volume per unit polymer mass are compared with fits using the Sanchez−Lacombe (SL) model[26−28] in Figure 3a,b. Pure-component lattice-fluid parameters for CO_2 and PMMA used in the SL equation of state (EoS) (characteristic temperature T^*, characteristic pressure p^*, and close-packed mass density ρ^*), as well as values for the lattice-fluid binary parameters (interaction energy parameter k_{ij} and volume interaction parameter η_{ij}) obtained from the fit of experimental data in Figure 3a,b, are reported in Table 1. Details on the experimental data and model correlation for high-pressure results using the SL lattice-fluid model have been previously reported.[15]

Whereas a good correlation of solubility and volume swelling can be obtained through the equilibrium thermodynamic analysis, by means of the lattice-fluid model, it is evident from the comparison in Figure 3a,b that the system volume at lower pressure (glassy region) exceeds the value predicted by the SL EoS. This is the effect of extra free volume that is frozen in the system below the glass transition temperature, and it is ultimately responsible for a pseudoequilibrium solute content that is higher than the equilibrium value predicted by the EoS.

A thermodynamic analysis of the pseudoequilibrium CO_2 solubility measured at low pressure, using the NET-GP approach, has already been published.[15] The present work is focused on the presentation and discussion of kinetic data related to differential sorption runs below the glass transition temperature and how the kinetic data compare to high-pressure differential sorption runs in the rubbery region.

Sorption Kinetics Experimental Data. For the purpose of distinguishing quantitatively between the high-pressure and low-pressure regions and applying the model described in the previous section to the latter, an evaluation of the threshold value for solute concentration at the glass transition was required. For this purpose, the results obtained by Sanchez and co-workers[29] for the solute concentration at the glass transition in the CO_2-PMMA system at different temperatures were used. From the reported data, a threshold value ω_g equal to 7.8% was taken as the solute fraction per unit polymer mass at the glass−rubber transition at 50 °C. In turn, by means of the SL EoS, the above value was recognized as the equilibrium CO_2 concentration in PMMA samples at 50 °C when in contact with pure gaseous CO_2 at 44 bar. The latter value, which is definitely consistent with the location of the discontinuity in the slope of a plot of polymer volume versus pressure in Figure 3b, was used as the glass transition pressure, P_g, for the system in what follows.
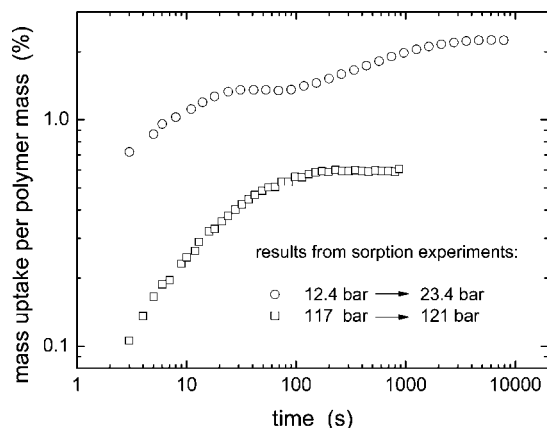
sensitivity of the chemical potential for the solute component, which, in turn, results in variations in the solubility and ultimately in the interface solute concentration at short times in the experiments as predicted by the boundary conditions in eqs 15.

Numerical Solution. To simplify the procedure for numerically solving the partial differential equation problem described by eqs 1−3, 9, 10, 14, and 15, a change in independent variables was used from laboratory-fixed to polymer-fixed coordinates.[8] As a result of the change in space variables, a moving boundary value problem is converted into a stationary boundary problem. The set of equations in the polymer-fixed coordinate system was discretized using the implicit control volume formulation of Patankar.[25] From the iterative solution of the resulting nonlinear algebraic equations, profiles of solute concentration and polymer density on spatial grid points at different times were obtained for the sorption problem of interest. The solute content and mass uptake in the film as functions of time were finally derived by convenient integration of the solute mass fraction over the film thickness.

Results and Discussion

Solubility/Dilation Experimental Data and Basic Thermodynamic Analysis. Figure 3a shows measured values for the equilibrium or pseudoequilibrium CO_2 content in a supported PMMA film at 50 °C in a sequence of differential pressure jump sorption experiments run in the QCM apparatus. Results for volume dilation in the same system measured in a similar

Figure 4. Experimental data on the kinetics of CO_2 sorption in a PMMA film for sorption steps from 12.4 to 23.4 bar and from 117 to 121 bar.

In view of the above discussion, sorption steps with a final pressure P^{fin} lower than P_g must be regarded as mass-transport processes in nonequilibrium glassy systems, whereas corresponding steps with an initial pressure P^{in} higher than P_g should be considered as run on equilibrium rubbery systems. Examples of experimental kinetic results for sorption steps in rubbery or glassy conditions are given in Figure 4, where data for mass uptake in the sorption step are reported as a function of time for increases in the CO_2 fluid-phase pressure both from 117 to 121 bar (sorption step in rubbery conditions) and from 12.4 to 23.4 bar (sorption step in glassy conditions).

For the first case, as for all other sorption steps above P_g, the process follows an elementary dynamic in which the amount of sorbed mass increases with time approximately following a power law with an exponent of $^1/_2$ up to 80% of the equilibrium value. With respect to what is expected for the case of diffusion-driven processes, deviations from a perfectly straight log−log plot are observed in the experimental results, which can be attributed to the effect of temperature variations in the early stages of the sorption process. Indeed, a temperature decrease registered at short time toward the set-point value induces both a modest reduction in the diffusion coefficient and a more relevant increase in the solubility of the solute component.

More complex results were obtained for the case of sorption steps below the glass transition pressure, with the data for a pressure increase from 12.4 to 23.4 bar in Figure 4 representing an example. The data show typical results of what is known as two-stage sorption. Two distinct stages can be recognized in the mass increase in this case, each characterized by different kinetic orders. An apparent steady state in the process is attained after a first sorption stage in which the mass uptake increases with time approximately following a power law with exponent $^1/_2$, as for the case in which the diffusive resistance rules the process. A second, slower sorption stage follows, which allows the system to further increase the solute content up to what is recognized as the pseudoequilibrium value for the imposed conditions of temperature, pressure, and solute fugacity. The second stage in the process is often referred to as the relaxation stage. The overall kinetics of the sorption process cannot be represented by means of a pure diffusion model. In the past decades, much evidence of two-stage sorption kinetics has been reported for the case of gas or vapor differential absorption into glassy polymers for different systems. It is important to observe, however, that two-stage kinetics is not characteristic of specific polymer−solute systems, as its occurrence is related to the amplitude of the fugacity increase for the solute in the sorption step and to the dimension of the polymeric sample. In fact, the

characteristic time for the diffusion process depends strongly on the sample dimension, whereas the characteristic time for the relaxation process is rather sensitive to the amplitude of the driving force represented by the fugacity jump in the sorption step. Furthermore, evidence of two-stage sorption kinetics can occur only for the case in which the characteristic time for the relaxation process is much larger than the characteristic time for the diffusion process. In the case of the sorption steps analyzed in this work, evidence of two-stage kinetics is favored by the rather small value of the film thickness (on the order of 1 μm), which results in an extremely low characteristic time for the diffusion process.

Two-stage sorption kinetics has received considerable attention in the past, and different attempts at modeling are reported in the literature. Several empirical models presented in this respect essentially follow the idea originally proposed by Long and Richman,[30] in which a pure Fickian diffusion model is coupled with a time-dependent boundary condition that directly accounts for a first-order variation of the interface concentration from a short-time value to a different long-term one.

The model proposed in the Theory section represents an effort to interpret, in consistent thermodynamic terms, the equation for boundary conditions proposed by Long and Richman.[30] Indeed, through the relaxation of the volume deformation in the polymer network, the model allows for a representation of the evolution in time of the interface solute concentration. During the sorption step, the latter changes from a value resulting from a phase equilibrium condition pertinent to the initial volume per unit polymer mass in the system up to that pertinent to the final V_p value reached at the end of the relaxation process for element A in the Voigt model here adopted. The variation in interface solute concentration is thus obtained in a straightforward fashion from the model, as a result of the description chosen for the volume relaxation process.

Results from Model Calculations. To use the model described above, the parameter χ was first evaluated using data already available for isothermal compressibility of pure PMMA determined in densification experiments. Using volume change data resulting from pressure variations in isothermal experiments in glassy and rubbery conditions by Bree et al.,[31] χ was estimated to equal 0.6 through eq 6. In accordance with available specific data for diffusivity in CO_2−PMMA system below the glass transition temperature,[32] the thermodynamic diffusion coefficient D_s in the model described above was set to a constant value of 1×10^{-7} cm^2/s, independent of the solute concentration. In fact, the diffusion coefficient for swelling penetrants in glassy polymers is rather sensitive to the solute concentration, and different diffusivity values were measured in several recent works on mass transport in the CO_2−PMMA system,[33−35] all lying in the range between 10^{-8} and 10^{-6} cm^2/s. However, finer tuning of the diffusivity value or allowing it to change with solute concentration in the mentioned range would be of no practical consequence in the comparison with experimental data in this particular case, as is evident in the discussion that follows. Finally, the specific volume of dry PMMA, V_p^0, was directly measured for the samples of interest as equal to 0.854 L^3/kg.

Based on the above evaluation of the parameter χ and the thermodynamic parameters in Table 1, the mass uptake as a function of time in a PMMA film for the sorption process induced by an increase in the solute fluid-phase pressure from the initial pressure P^{in} to the final pressure P^{fin} can finally be obtained by the model when a suitable value of the bulk viscosity η^* is known, for the case in which pure isothermal conditions are assumed. In the calculations performed in this
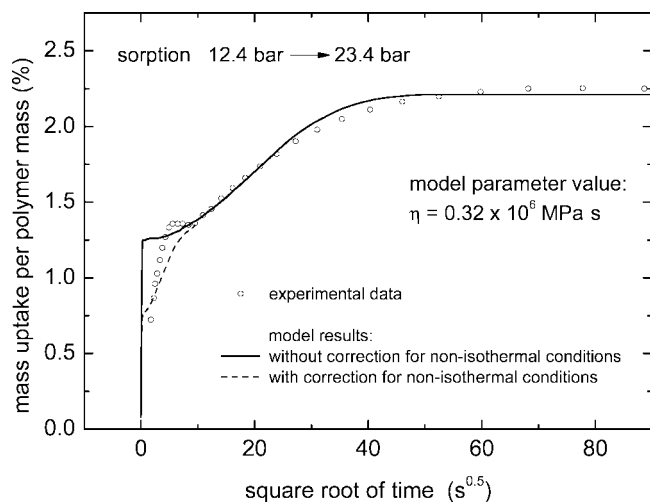
Figure 5. Kinetics of CO_2 sorption in a PMMA film for a sorption step from 12.4 to 23.4 bar. Comparison of experimental values with model results.

Table 2. Values for Model Parameter (η^*) from Fitting of Experimental Sorption Data

pressure limits in sorption step (bar)	bulk viscosity η^* (MPa s)
$12.4 \rightarrow 23.4$	0.32×10^6
$21.4 \rightarrow 27.9$	1.2×10^6
$25.4 \rightarrow 33.1$	1.1×10^6

work, the latter model parameter was fit to experimental data in any sorption step, assuming that a constant value holds for the entire concentration range in the step. Results of this effort are shown as a solid line in Figure 5 for the case of $P^{in} = 12.4$ bar and $P^{fin} = 23.4$ bar. The values used for η^* in this correlation are reported in Table 2. It must first be noted that the model allows for a correct representation of the two-stage sorption behavior observed in the experiment. Indeed, the latter easily emerges from the solution of the set of model equations for the case $T < T_g$ in all cases in which the characteristic time for the diffusion process, t_D ($\sim \delta^2/D_s$), is significantly lower than that of the volume relaxation process, t_R ($\sim \eta^*/\Delta P^{eq}$). The comparison between model calculations and experimental results allows for the recognition that the amount of CO_2 absorbed in each of the two steps is satisfactorily described by the model. The latter results are particularly significant as they are independent of the specific value used for the fitting parameter η^*. Indeed, the solute contents reached in first and second sorption steps are purely predictive results obtained from the use of the model, and they essentially rely on the description of the thermodynamic properties obtained through the NET-GP model for glassy polymers and on the correct values of the initial and final volumes for the system in the given sorption step. It must then be observed that a proper choice of the model parameter η^* also allows, in this case, for a satisfactory representation of the kinetics of the second stage in the sorption process. On the other hand, the calculation largely underestimates the characteristic time of the first sorption step, and it must be said that no diffusivity value for D_s in the range observed for the same polymer–penetrant pair in previous works (10^{-8}–10^{-6} cm²/s), would allow for model predictions that get close to the experimental results in this respect. To appreciate the role that the nonisothermal conditions resulting in the early stage of the experiment play in the sorption process, model calculations were also performed for the same jump in the solute pressure and with the same model parameters, but allowing the system temperature to emulate the variations measured for the gas-

Table 3. Characteristic Values of Temperature Deviation at Short Times in Sorption Steps

pressure limits in sorption step (bar)	ΔT (K)	t^* (s)
$12.4 \rightarrow 23.4$	5.0	20
$21.4 \rightarrow 27.9$	2.0	20
$25.4 \rightarrow 33.1$	2.0	20

phase temperature. To this end, the expression for the system temperature in eq 16 was used, with values of the temperature jump, ΔT, and characteristic time, t^*, obtained from experimental evidence related to the gas phase in the sorption cell. Specific values measured for ΔT and t^* are reported in Table 3. Results from a model simulation performed according to the mentioned simplified correction for nonisothermal conditions are also reported in Figure 5 as a dashed line. In the model calculations, the temperature rise reduces the polymer-phase CO_2 concentration, as an effect of the decrease in solubility, and this ultimately results in a smaller magnitude of the fast jump to a first uptake exhibited by the temperature-corrected model predictions, when compared to the corresponding jump calculated through the isothermal model. Following the first jump, a more gradual mass uptake occurs in the model predictions, although it is still rapid when compared to long-time behavior, which reflects the temperature decrease toward the set-point value and ultimately results in an increase in the polymer-phase CO_2 concentration. It clearly appears from the data in Figure 5 that the amount and characteristic time for deviations of the experimental data from the predictions of the isothermal model are definitely consistent with the effect of temperature deviations on the sorption process. Indeed, although the temperature evolution in the system is taken into account in highly simplified terms in the latter calculation, the comparison with experimental data allows for the conclusion that this effort points to the phenomenon that actually drives the kinetics of the first stage in the sorption process.

Further comparisons between model results and experimental data for sorption kinetics in the same solute–polymer system are provided in Figures 6 and 7, where sorption steps at 50 °C from 25.4 to 33.1 bar and from 21.4 to 27.9 bar, respectively, are reported. Also in these cases, the solid lines refer to the best fit of the experimental data by means of the model for isothermal conditions in which the only parameter η^* was treated as adjustable, whereas the dashed lines reflect results from the same model when the simplified correction in eq 16
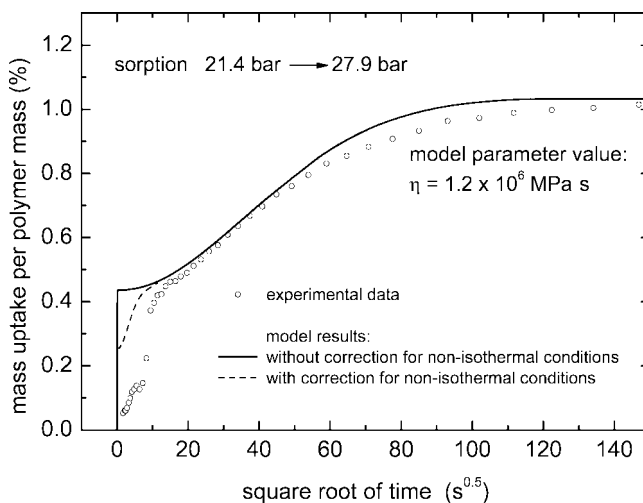

Figure 6. Kinetics of CO_2 sorption in a PMMA film for a sorption step from 25.4 to 33.1 bar. Comparison of experimental values with model results.
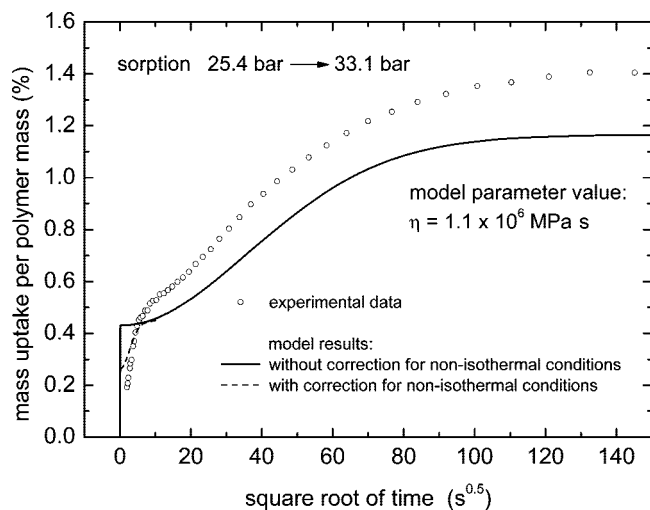
Figure 7. Kinetics of CO_2 sorption in a PMMA film for a sorption step from 21.4 to 27.9 bar. Comparison of experimental values with model results.

Figure 8. Model results for the kinetics of CO_2 mass ratio increase in PMMA at the film interface for a sorption step from 12.4 to 23.4 bar.

to account for nonisothermal conditions is adopted, after measurements for temperature in the gas phase. The values used in these calculations for the bulk viscosity η^* and the parameters used in the correction for nonisothermal conditions are reported in Tables 2 and 3, respectively. Comments on the comparison between the model calculation and the experimental results for the two latter cases can be made that are similar to those expressed for the previous step. The model confirms its ability in predicting the amount of mass absorbed in single stages of the sorption process, and it allows a satisfactory representation of the second-stage kinetics to be obtained through the use of a convenient value for the bulk viscosity, of the same order as that retrieved for the previous case. On the other hand, whereas predictions from the model for isothermal conditions do not show a characteristic time consistent with that measured for the first stage in the sorption process, the simple correction used for nonisothermal conditions allows a reasonable approximation of the experimental evidence in this respect to be obtained.

A closer look is warranted by the variation in time of the solute concentration at the interface between the gaseous and polymeric phases as predicted by the model for the cases considered in this work, which ultimately results from the time variation of the volume per unit polymer mass of sample elements at the same interface. In Figure 8, results are shown for the variation in interface solute mass ratio for the sorption step from 21.4 to 27.9 bar, as calculated in the model simulation. It can be appreciated from a comparison of the data in Figures 5 and 8 that the variation in the solute concentration due to the variation in volume is approximately 40% of the overall increase in the solute concentration in this step and that this variation follows approximately first-order kinetics. The latter observation is consistent with the key assumption in the empirical model by Long and Richman[30] for anomalous sorption in glassy polymers. On the other hand, it must be considered that the model results recover the interface effect described in the Long−Richman (LR) model through the adoption of a local relaxation law that is valid in any of the polymeric elements in the sample. It should also be observed, in this respect, that, whereas the LR model makes use of empirical parameters for which no independent procedure of estimation is available, the model introduced in this work considers only one adjustable parameter (η^*) that refers to a specific property of the polymer matrix. Indeed, the adjustable parameter in the model proposed
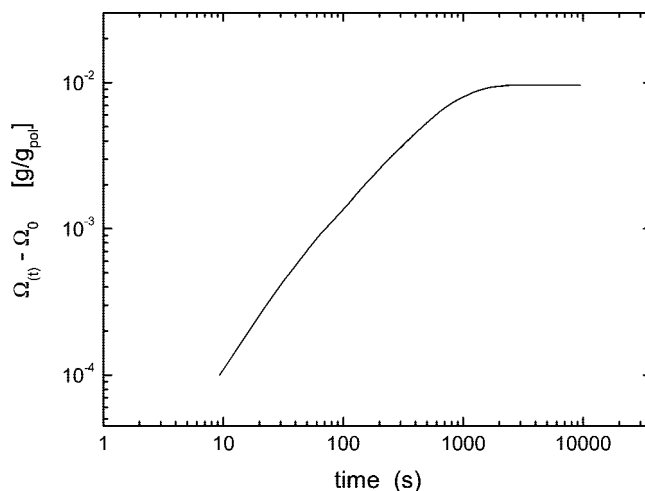
here has a precise physical meaning, and comments on the values resulting from the fitting procedures discussed above are in order. In all cases considered in this work, a value of the characteristic bulk viscosity for Voigt element A on the order of 10^{12} Pa s was obtained. Although comparison of data for η^* retrieved in this work with glassy PMMA bulk viscosity estimated through direct mechanical measurements is not possible in view of the lack of the latter type of data, it can be safely said that the order of magnitude of the model parameter η^* obtained here is entirely consistent with literature values for the short-time shear viscosity of PMMA below the glass transition temperature.[36] The short-time bulk viscosity is also expected to change with solute concentration and volume deformation, and the non-negligible variations in bulk viscosity η^* obtained in this work from the analysis of differential sorption processes with different pressure jumps are likely the result of its complex dependence on the state of the polymeric mixture and, in more general terms, on the nonlinear effects in the viscoelastic behavior of the system that are not taken into account here.

Conclusions

A thermodynamic model is presented that is aimed at interpreting the relation between the diffusion of swelling agents and volume relaxation in glassy polymers. The model is based on a thermodynamic analysis of the properties of glassy polymeric mixtures based on the nonequilibrium thermodynamics (NET-GP) approach. The volume relaxation process is thus represented through a simplified model for the bulk rheology of the polymer network. The two-Voigt-element model considered here for volume relaxation allows for the distinct representation of true thermodynamic equilibrium conditions for the polymeric material (corresponding to the case of negligible residual viscous stress in both Voigt elements) and to pseudoequilibrium conditions (pertinent to the case of negligible viscous stress in only the Voigt element characterized by a short relaxation time). It must be stressed here that the picture of bulk rheology behavior offered through this model is simplified in many respects, as it accounts for only one characteristic time in volume relaxation and it is limited to the description of earlier stages in the relaxation process for the glassy matrix. In fact, the volume recovery phenomenon in glassy systems is highly nonlinear, and a comprehensive model for its representation should also account for the different apparent compressibilities

and relaxation times measured for compression and expansion experiments.[24] Calculations presented in this work as application of the model are limited to the analysis of short-term effects of moderate pressure jumps inducing positive swelling phenomena. The comparisons with experimental results are aimed to verify that the model offers a correct physical picture of the swelling phenomena, and the implementation of a more complete description of bulk rheology is left to future developments in the analysis.

Despite its simplicity, when coupled with a generalized Fick's law for the diffusive flux of the penetrant species, the model is able to represent the two-stage sorption behavior, typically observed for kinetics of differential sorption experiments in relatively thin glassy polymer films. A procedure is discussed for the evaluation of specific model parameters on the basis of available data for isothermal compressibility for pure the polymer in glassy and rubbery states. Through the description of volume relaxation phenomena, the model is able to represent the variation in time of the solute concentration at the sample interface when a constant value for solute fugacity is assured by boundary conditions. The latter can be compared to assumptions made in the well-known empirical model by Long and Richman,[30] and it can be stated that the model introduced in this work allows for the prediction of one of the parameters in the LR model and for a specific interpretation of the second parameter. Indeed, the model is able to predict the amplitude of the initial jump in the solute concentration at the interface with respect to that attained at long times, and it allows the characteristic time of variation for the interface concentration to be interpreted as the corresponding time for volume recovery in the system.

Results from model calculations were compared with experimental data for the sorption kinetics of CO_2 in glassy PMMA supported films. The two-stage sorption kinetics observed for the experimental data was correctly represented by means of the simple thermodynamic model discussed herein. In particular, the model allows for the satisfactory prediction of the final solute uptake in both the short-time and long-time stages of the sorption process. The experimental data for the kinetics of the relaxation-driven stage is then correctly represented in model calculation by means of values for the bulk viscosity of the polymer that are consistent with the results for the pure-polymer shear viscosity.

To allow for a complete discussion of the experimental data of sorption kinetics retrieved in this work, a simplified analysis was also performed to address the problem of intrinsic nonisothermal conditions of the sorption process at early stages, and this ultimately allowed for the conclusion that, in view of the extremely low thickness of the samples used in the experiments, which results in an extremely low value of the characteristic time for the pure diffusion process, the kinetics of the first sorption stage in this case is mostly driven by the temperature variation in the sorption cell.

Acknowledgment

Notation

D_s = thermodynamic diffusion coefficient for solute mass flux in the solute−polymer mixture

f_s = solute fugacity in the solute−polymer mixture

f_{s_g} = solute fugacity in the solute−polymer mixture at the glass transition

k_g^- = glassy-state pure-polymer isothermal compressibility at the glass transition temperature

k_g^+ = rubbery-state pure-polymer isothermal compressibility at the glass transition temperature

j_s = diffusive solute flux in the solute−polymer mixture (as defined in eq 11)

j_{s_x} = out-of-plane component of the diffusive solute flux in the solute−polymer mixture

P = absolute pressure

P_g = solute-species pressure in the gas phase at the glass transition

P^{in} = solute-species pressure prevailing in the gas phase before the sorption step

P^{fin} = solute species pressure prevailing in the gas phase during the sorption step

P^{EQ} = equilibrium pressure

p_i^* = characteristic pressure in the SL EOS for component i

R = gas constant

t = elapsed time

T = absolute temperature

T_g = pure-polymer glass transition temperature

T_{gmix} = glass transition temperature in the solute−polymer mixture

T_i^* = characteristic temperature in the SL EOS for component i

$\underline{v}_p$ = velocity of the polymeric species in the solute−polymer mixture

v_{p_x} = out-of plane component of the velocity of the polymeric species in the solute−polymer mixture

$\underline{v}_s$ = velocity of the solute species in the solute−polymer mixture

V_{pol} = pure-polymer specific volume

V_p = volume per unit polymer mass in the solute−polymer mixture

V_p^0 = pseudoequilibrium volume per unit polymer mass in the solute−polymer mixture at infinite dilution (corresponding to the pure-polymer specific volume in the glassy state)

V_p^A, V_p^B = volume per unit polymer mass in Voigt elements A and B, respectively, in Figure 1

$\overline{V}_p^B$ = constant value of volume per unit polymer mass in Voigt element B specified in eq 7

V_p^{EQ} = equilibrium volume per unit polymer mass in the solute−polymer mixture

V_p^{PE} = pseudoequilibrium volume per polymer mass in the solute−polymer mixture

x = spatial coordinate in the out-of-plane direction

δ = film thickness

η^A, η^B = bulk-viscosity Voigt elements A and B, respectively, in Figure 1

η^* = model parameter for short-term bulk viscosity in the glassy polymeric system

η_{ij} = volume-interaction binary coefficient in the SL EOS for the pair of components $i-j$

k_{ij} = interaction-energy binary coefficient in the SL EOS for the pair of components $i-j$

μ_s = solute chemical potential in the solute−polymer mixture

μ_s^{NE} = nonequilibrium solute chemical potential in the solute−polymer mixture

μ_s^0 = pure-component solute chemical potential

ρ_s = solute mass per unit volume in the solute−polymer mixture

ρ_p = polymer mass per unit volume in the solute−polymer mixture

ρ_i^* = characteristic density in the SL EOS for component i

χ = weighting factor for the rheological model (see eq 1)

Ω = solute mass ratio at the interface

$\Omega_0 = \lim_{t \to 0^+} \Omega_{(t)}$ = solute mass ratio established at the interface at the beginning of the sorption process

ω_s = solute mass fraction in the solute−polymer mixture

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