

Sorption Thermodynamics and Mutual Diffusivity of Carbon Dioxide in Molten Polycaprolactone

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Solution thermodynamics and mutual diffusivity of the system carbon dioxide–molten poly(ϵ -caprolactone) (PCL) have been investigated experimentally in the temperature range 70–85 °C and at pressures up to 6.5 MPa. Sorption data have been interpreted on the basis of Sanchez–Lacombe lattice theory. Sanchez–Lacombe parameters for pure PCL have been evaluated by fitting experimental pressure–volume–temperature data obtained by using a high-pressure dilatometer, while parameters for carbon dioxide have been taken from the literature. Information on the free volume of the mixture, as gathered from the solution thermodynamics analysis, has been used in the classical free-volume theory proposed by Duda and Vrentas to fit mutual diffusivity data, obtained from sorption kinetics experiments.

Introduction

Biodegradable polymers have found many applications in medicine and pharmaceutical technology, but the use in commodity applications (garbage bags, food and beverage containers, and packaging) is limited because of their higher cost and, more often, because of their low performances in terms of final properties and/or processability.

An interesting application field of biodegradable polymers is that of foams, with particular reference to foams for packaging applications, where the environmental issue is relevant. In fact, because of their peculiar properties, cellular polymers are attractive when coupling of good functional properties with a low weight is needed, as is the case of acoustic insulation and damping, thermal insulation, and impact resistance. In general, foams are produced using a blowing agent that can act by a chemical or physical mechanism. In the first case, a chemical transformation of an additive causes a large evolution of gaseous molecules that can solubilize and diffuse in the polymer melt. In the second case, a blowing agent is directly injected, in the liquid or gaseous state, into the extruder, where the thermodynamic conditions promote the formation of the molten polymer–gas mixture. Physical foaming agents, if properly selected, are characterized by a potentially low environmental impact.

To form a polymeric foam from a polymer–gas mixture, bubbles must first nucleate and then grow within the molten or plasticized viscoelastic material as a result of the diffusion of solubilized gas molecules into the bubble volume. Subsequently, setting of the structure occurs as a consequence of the viscosity

increase during cooling and/or reduction of plasticization, leading to the final solidification of the continuous phase.

As a consequence, solubility and diffusivity in the molten polymer are among the most important properties of a gaseous foaming agent in determining the foam structure. In particular, gas solubility determines the extent of the plasticization effect on the polymer and the final density of the foam and is one of the primary concerns when choosing physical blowing agents in a foam extrusion process.¹ On the other hand, blowing agent–polymer mutual diffusivity affects the bubble nucleation and growth phenomena while, from the processing point of view, diffusion fixes the residence time and the cooling rates on the extruded foam needed to avoid cell collapse.

Solubility and diffusivity are significantly affected by the nature of the components, the concentration of the foaming agent, and, obviously, operating temperatures and pressures.^{2,3}

Several theories are available in the literature to describe the thermodynamic equilibrium of gas–polymer mixtures. Among them, the relatively simple Sanchez–Lacombe (SL) lattice fluid (LF) model has supplied good results for the case of gas sorption in molten polymers, as reported by several authors.^{4–6} Hariharan et al.⁷ have critically examined the ability of the SL equation of state (SL EOS) to predict the solubility of a small penetrant in rubbery polymer matrices, evidencing how the predicted isotherms strongly depend on solute EOS parameters and on the mixing parameter for polymer–penetrant interactions.

On the other hand, mass transport properties of low molecular weight compounds in polymers have been successfully described by using free-volume theories,^{8,9} according to which mass transport is controlled by the availability of the free volume within the system.

In this work we analyze the sorption and transport properties of CO₂, which can be used as a foaming agent, in a biodegradable and compostable polyester, poly(ϵ -

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caprolactone) (PCL). The solubility and diffusivity of the expanding gas at different pressures and temperatures into molten PCL were measured at several pressures (up to 6.5 MPa) and at temperatures ranging from 70 to 85 °C. Pressure–volume–temperature (*PVT*) characterization of PCL was also performed. This allowed the prediction of the thermodynamic behavior (sorption isotherms) of the mixture in a wide range of operative pressures and temperatures by using the SL EOS. Information on the volumetric behavior of the mixture based on SL EOS was used to evaluate the relevant free-volume parameters that were needed to interpret mutual diffusivity data according to the free-volume approach proposed by Vrentas and Duda.^{8,9}

Theoretical Background

EOSs of Molten Polymers. Several empirical and theoretical EOSs have been proposed in the literature to describe equilibrium *PVT* behavior of molten polymers.^{10,11}

Among these, the Tait equation¹² is the most widely used empirical equation for modeling *PVT* data of polymers. Although it was not originally developed for polymers but for seawater, it has been successfully applied to a wide variety of polymeric liquids,^{10,13} showing accurate reproduction of *PVT* data. The Tait equation relates the specific volume, \hat{V} , to pressure, P , and temperature, T , in terms of the zero-pressure volume, $\hat{V}(0, T)$, and of the parameters, $B(T)$ and C , through the following expression:

$$\hat{V}(P, T) = \hat{V}(0, T) \{1 - C \ln[1 + P/B(T)]\} \quad (1)$$

The parameter C is often taken to be constant and equal to 0.0894.¹³ $B(T) = B_0 \exp(-B_1 T)$ and $\hat{V}(0, T) = A_0 + A_1 T + A_2 T^2 + A_3 T^3$ are temperature-dependent functions containing material parameters. Although the Tait equation has the advantage of being simple, it does have, however, a mathematical deficiency:¹⁴ at sufficiently high pressure, it predicts a negative volume, which is obviously not physically possible.

Each of the various theoretical EOSs proposed in the literature is based upon a particular molecular description of the polymeric system (the molecular configurations and the associated energy states).¹⁵ The substantial difference among the various EOS models is the specific idealization of the molecular structure of the polymer. Cell model EOS,^{16–18} Flory–Orwoll–Vrij EOS,¹⁹ SL EOS,²⁰ and Simha–Somcynsky EOS²¹ are some of the most relevant examples.

In particular, the SL EOS is a LF theory, where holes (i.e., vacant cells) are introduced in the polymer lattice in order to provide additional disorder to the regular spatial configuration of the molecules. In this model, the volume change of the system is due to the change of the holes concentration. The SL EOS has the following expression:

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}[\ln(1 - \tilde{\rho}) + (1 - 1/r)\tilde{\rho}] = 0 \quad (2)$$

where r is the number of lattice sites occupied by a fluid molecule and $\tilde{\rho}$, \tilde{P} , and \tilde{T} are reduced density, pressure, and temperature ($\tilde{\rho} = \rho/\rho^*$; $\tilde{T} = TT^*$; and $\tilde{P} = P/P^*$) and ρ^* , P^* , and T^* are model parameters.

SL LF Theory for Polymer Mixtures. Sanchez and Lacombe extended their LF theory to the case of mixtures by adopting appropriate mixing rules. The

EOS of the mixture is formally identical with the EOS of a pure fluid:²²

$$\tilde{\rho} = 1 - \exp\left[-\frac{\tilde{\rho}^2}{\tilde{T}} - \frac{\tilde{P}}{\tilde{T}} - \left(1 - \frac{\phi_1}{r_1}\right)\tilde{\rho}\right] \quad (3)$$

where ϕ_1 is the volume fraction of the solute defined as

$$\phi_1 = \frac{\frac{\omega_1}{\rho_1^*}}{\frac{\omega_1}{\rho_1^*} + \frac{\omega_2}{\rho_2^*}}$$

In eq 3 $\tilde{\rho}$, \tilde{P} , and \tilde{T} are now defined with reference to polymer–solute mixture parameters, which are related to SL EOS parameters for pure components through the following mixing rules:²³

$$P^* = \phi_1 P_1^* + \phi_2 P_2^* - \phi_1 \phi_2 \Delta P^* \quad (4)$$

with $\Delta P^* = P_1^* + P_2^* - 2P_{12}^*$ and $P_{12}^* = \psi \sqrt{P_1^* P_2^*}$

$$T^* = \frac{P^*}{\frac{\phi_1 P_1^*}{T_1^*} + \frac{\phi_2 P_2^*}{T_2^*}} \quad (5)$$

$$\frac{1}{\rho^*} = \frac{\omega_1}{\rho_1^*} + \frac{\omega_2}{\rho_2^*} \quad (6)$$

where ψ is the mixing parameter (it measures the deviation from the empirical geometric mean combination rule) and ω_i is the mass fraction of component i . Here and in the following, subscript 1 refers to the penetrant and subscript 2 to the polymer.

Once the EOS parameters of pure components are known, the SL EOS parameters for the mixture are directly predictable if the geometric mean combination rule is assumed for P_{12}^* (i.e., $\psi = 1$).

An expression for the chemical potential of penetrant (μ_1) in the penetrant–polymer mixture can be determined on the basis of the expression obtained by Sanchez and Lacombe²³ for the Gibbs free energy of the mixture:

$$\frac{\mu_1}{kT} = \ln \phi_1 + \left(1 - \frac{r_1}{r_2}\right)(1 - \phi_1) + r_1^0 \tilde{\rho} X_1 (1 - \phi_1)^2 + \left[-\frac{\tilde{\rho}}{\tilde{T}_1} + \frac{\tilde{P}_1}{\tilde{T}_1 \tilde{\rho}_1} + \frac{(1 - \tilde{\rho}) \ln(1 - \tilde{\rho})}{\tilde{\rho}} + \frac{\ln \tilde{\rho}}{r_1^0}\right] r_1^0 \quad (7)$$

where

$$X_1 = \Delta P^* v_1^*/kT$$

In the previous expressions, r_i represents the number of sites that a molecule of component i occupies in the solution lattice, r_i^0 is the number of sites that a molecule of penetrant occupies in the pure state lattice, and v_1^* is the close-packed volume of a mer of penetrant in the pure state.

The best results in modeling sorption isotherms by the SL EOS approach are attained when both polymer and penetrant EOS parameters are determined from pure-component properties in the same temperature and pressure ranges as those for the sorption data.

Furthermore, ψ can be used as a fitting parameter of experimental solubility data: in fact, its value is likely to be different from 1 in the case of mixture components characterized by different types of interaction energies.

Evaluation of Sorption Isotherms Using the SL Model. From the expressions introduced by Sanchez and Lacombe for the EOSs and for the chemical potentials, the evaluation of sorption isotherms of penetrant in molten polymers is straightforward. In fact, on the basis of the SL theory, at fixed temperature and pressure, for a pure penetrant in contact with a polymer–penetrant mixture, equilibrium values for reduced densities and penetrant mass fractions can be obtained from the following equations:

I. EOS for pure penetrant (eq 2).

II. EOS for penetrant–polymer mixture (eq 3).

III. Equality of the chemical potential between the pure penetrant phase and the penetrant–polymer mixture:

$$\left[-\frac{\tilde{p}_1}{\tilde{T}_1} + \frac{\tilde{P}_1}{\tilde{T}_1\tilde{\rho}_1} + \frac{(1-\tilde{\rho}_1)\ln(1-\tilde{\rho}_1)}{\tilde{\rho}_1} + \frac{\ln\tilde{\rho}_1}{r_1^0} \right] = \ln\phi_1 + 1 - \phi_1 + \tilde{\rho}_1^0 X_1(1-\phi_1)^2 + \left[-\frac{\tilde{p}}{\tilde{T}_1} + \frac{\tilde{P}_1}{\tilde{T}_1\tilde{\rho}} + \frac{(1-\tilde{\rho})\ln(1-\tilde{\rho})}{\tilde{\rho}} + \frac{\ln\tilde{\rho}}{r_1^0} \right] r_1^0 \quad (8)$$

How close the sorption isotherms predicted on the basis of this approach to experimental data are strongly depends on the adopted parameters for the penetrant EOS.⁷ In fact, different penetrant parameters lead to relevant differences in the values of the penetrant phase chemical potential (left-hand side of eq 8) and, consequently, of the predicted sorption levels.

Free-Volume Theory for Self-Diffusivity and Mutual Diffusivity of Low Molecular Weight Penetrants in Molten Polymers. The diffusion of low molecular weight compounds in polymer melts can be interpreted on the basis of free-volume theories. In fact, mass transport of small penetrants in molten polymers can be assumed to proceed by means of uncorrelated consecutive jumps in random directions: a successful diffusive jump occurs when local density fluctuations promote the opening of a free-volume hole of a size suitable for the molecule to jump in and when polymer strands are quickly recompacted behind the molecule, preventing it from jumping back. The free volume involved in the diffusion mechanism is assumed to be freely redistributed inside the sample and, in general, no energy barriers are assumed to be associated with the single jump.

Starting from the results of Bearman,²⁴ Duda et al.²⁵ obtained an expression of the mutual diffusivity coefficient as a function of self-diffusivities of the penetrant and polymer, D_1 and D_2 , in the following instances:

(1) It is assumed that

$$\zeta_{12} = (\zeta_{11}\zeta_{22})^{1/2}$$

where ζ_{11} , ζ_{22} , and ζ_{12} are the penetrant–penetrant, polymer–polymer, and penetrant–polymer friction coefficients, (2) trace amounts of penetrant are considered ($\omega_1 \ll 1$), (3) the physically sound hypothesis $D_1 \gg D_2$ is adopted, and (4) the behavior of ζ_{11} and of ζ_{22} is reasonable.⁸ The expression for the mutual diffusivity,

D , takes the following form:

$$D = D_T \frac{\rho_2 \rho_1 \hat{V}_2}{RT} \left(\frac{\partial \mu_1}{\partial \rho_1} \right)_{T,P} \quad (9)$$

where $D_T = D_1/(1 - D_1/D_1^*)$, $D_1^* = RTM_1/\rho_1\zeta_{11}N_A^2$, ρ_i = mass density of component i , \hat{V}_2 = partial specific volume of the polymer, R = gas constant per mole, and N_A = Avogadro's number.

For a trace amount of penetrant, $D_1/D_1^* \approx 0$ and, hence, $D_T \approx D_1$. As a consequence, from eq 9 it can be easily obtained⁹ that

$$D = \frac{D_1 \rho_1 \rho_2 \hat{V}_2}{RT} \left(\frac{\partial \mu_1}{\partial \rho_1} \right)_{T,P} = \frac{D_1 \omega_1 \omega_2}{RT} \left(\frac{\partial \mu_1}{\partial \omega_1} \right)_{T,P} \quad (10)$$

which, in turn, can be expressed in terms of the free-volume theory^{8,9,26} as

$$D = D_{01} \exp\left(-\frac{\gamma(\omega_1 \hat{V}_1^* + \xi \omega_2 \hat{V}_2^*)}{\hat{V}_{FH,M}} \right) \frac{\omega_1 \omega_2}{RT} \left(\frac{\partial \mu_1}{\partial \omega_1} \right)_{T,P} \quad (11)$$

Here the preexponential factor, D_{01} , is assumed to be temperature-independent. γ is a numerical factor, generally ranging from 0.5 to 1, that accounts for possible superposition of the free-volume elements. $\hat{V}_{FH,M}$ represents the average specific hole free volume of the mixture. Its value depends on the absolute pressure, temperature, and composition of the mixture (\hat{V}_{FH} represents the so-called *hole free volume*,²⁶ which is associated with holes and vacancies discontinuously distributed in the material at any instant of time and has no redistribution energy: this is the fraction of specific free volume that is assumed²⁶ to be involved in the diffusive jumps).

\hat{V}_1^* and \hat{V}_2^* represent the critical specific hole free volume that should be available in the system to allow for respectively the diffusive jump of a subunit of the penetrant and of the polymer.

ξ is defined as

$$\xi = \frac{\tilde{V}_{1J}^*}{\tilde{V}_{2J}^*} = \frac{\hat{V}_1^* M_{1J}}{\hat{V}_2^* M_{2J}} \quad (12)$$

where \tilde{V}_{iJ}^* is the critical volume for a jumping subunit of component i per mole of jumping subunits of component i and M_{iJ} represents the molecular weight of the jumping subunit of component i . In the case of small penetrants, M_{1J} is frequently taken as the penetrant molecular weight, M_1 .

The term $(\partial \mu_1 / \partial \omega_1)_{T,P}$ present in eqs 10 and 11 can be evaluated from SL EOS parameters as follows:

$$\left(\frac{\partial \mu_1}{\partial \omega_1} \right)_{T,P} = \left(\frac{\partial \mu_1}{\partial \phi_1} \right)_{T,P} \left(\frac{\partial \phi_1}{\partial \omega_1} \right)_{T,P} \quad (13)$$

The term $(\partial \mu_1 / \partial \phi_1)_{T,P}$ can be evaluated by using the following expression derived by Sanchez and Lacombe:²³

$$\left(\frac{\partial \mu_1}{\partial \phi_1} \right)_{T,P} = 2kTr_1\phi_2 \left\{ \frac{1}{2} \left[\frac{1}{r_1\phi_1} + \frac{1}{r_2\phi_2} \right] - \tilde{\rho} \left[X + \frac{1}{2} \delta^2 \tilde{TP}^* \beta \right] \right\} \quad (14)$$

with

$$\delta \equiv \bar{\rho} \frac{d\left(\frac{1}{\bar{T}}\right)}{d\phi_1} - \frac{d\left(\frac{1}{r}\right)}{d\phi_1} + \bar{v} \frac{d\left(\frac{\bar{P}}{\bar{T}}\right)}{d\phi_1}$$

$$\bar{T}P^*\beta = \bar{v} \left[\frac{1}{\bar{v}-1} + \frac{1}{r} - \frac{2}{\bar{T}} \right]^{-1}$$

$$X = \frac{\Delta P^* \bar{v}^*}{kT} \quad \bar{v} = 1/\bar{\rho}, \quad r = \sum x_i r_i$$

where x_i is the molar fraction of component i and \bar{v}^* is the average close-packed mer volume in the mixture (it is obviously the same for both components 1 and 2). In the present investigation, $1/r_2^0$ has been assumed to be equal to zero and the values adopted for ψ to evaluate ΔP^* were obtained, at each temperature, from data fitting of sorption isotherms with SL EOS.

Finally, the term $(\partial\phi_1/\partial\omega_1)_{T,P}$ can be evaluated from the following equation:

$$\left(\frac{\partial\phi_1}{\partial\omega_1}\right) = \frac{(\rho_1^* \rho_2^*)^{-1}}{\left[\frac{1}{\rho_2^*} + \left(\frac{1}{\rho_1^*} - \frac{1}{\rho_2^*}\right)\omega_1\right]^2} \quad (15)$$

Experimental Section

Materials. PCL was supplied by Solvay Interlox Ltd., U.K. (PCL CAPA 6800). Before use, the samples were vacuum-dried at 40 °C for 24 h. High-purity-grade CO₂ was obtained from Società per l'Ossigeno Liquido (SOL, Monza, Italy) and used as received. The glass transition temperature (T_g) and the melting temperature (T_m) as determined by differential scanning calorimetry (DSC; see below) were respectively -62 and +58 °C. The number-average molecular weight (M_n) was 69 000 ± 1500, the weight-average molecular weight (M_w) was 120 000 ± 2000, and the polydispersity index (M_w/M_n) was equal to 1.74.

Dilatometry. The *PVT* behavior of PCL has been evaluated by performing isothermal measurements at pressures up to 200 MPa and temperatures from 25 to 120 °C with a GNOMIX (Boulder, CO) high-pressure dilatometer. Measurements have been performed using the classical bellows technique, in which pressure is applied to the samples through a confining fluid (mercury) and the volume is measured by a linear variable differential transformer mounted beneath the pressure vessel. The measurements procedure is described in detail elsewhere.²⁷

CO₂ Sorption Experiments. Sorption experiments were conducted by measuring changes of the sample weight with a calibrated quartz spring microbalance (RUSKA Co., Houston, TX; maximum elongation of 400 mm, maximum weight of 50 mg) placed in a pressurized stainless steel cylindrical vessel (2.54 cm diameter) equipped with high-pressure viewing ports and with a water jacket for accurate temperature control. The upper spring hook was connected to the VCR plug used to close the vessel. The measuring cell was connected with service lines to a flask, to a pressure transducer (TransInstruments BHL-4240-01-01M0-65; maximum pressure of 10 MPa, accuracy of ±0.005 MPa), to the gas cylinder, and to a high-vacuum turbomolecular pump. The polymer sample was placed in an aluminum pan (which guaranteed the dimensional stability of the sample) and hanged to the lower spring hook. The aluminum pan had a cylindrical shape, and its dimen-

sions were accurately measured. The initial thickness of the molten polymer was evaluated on the basis of its density at the temperature of interest (as calculated from *PVT* measurements), of the weight of the sample, and of the diameter of the pan. Thickness changes of the sample due to dissolution of carbon dioxide were taken into account in data analysis, as reported afterward. Kinetics of CO₂ sorption and sorption equilibrium values in the molten polymer were evaluated by measuring the spring elongation with a traveling microscope (resolution equal to 0.01 mm). To ensure the measurement of the absolute spring elongation, an undeformable reference glass rod, coaxial to the spring helix, was used.

In a typical experiment, 30 mg of polymer was first vacuum-dried (10⁻³ Torr) at the test temperature until a constant weight was attained. At all of the investigated temperatures (70, 75, and 85 °C), samples were in the molten state. Measurements were conducted by performing step-change sorption experiments. Consecutive sorption tests were conducted by step-increasing the carbon dioxide pressure (about 0.3 MPa steps) with preheated carbon dioxide, after the attainment of equilibrium sorption in the previous step. When the penetrant diffusivity is expected to depend on the penetrant concentration, data should be properly analyzed to derive meaningful diffusion coefficients for step-change tests. In this investigation, we adopted a method proposed by Vrentas et al.²⁸ to obtain the value of mutual diffusivity at some penetrant concentration, comprised between initial and final concentrations of each sorption test. The method is based on the evaluation of an average mutual diffusivity (\bar{D}) from the initial rate of sorption. Because the system under investigation follows a Fickian²⁹ behavior, the expression for \bar{D} takes the form

$$\bar{D} = \frac{\pi L^2}{4} \left(\frac{d(M_t/M_\infty)}{d(\sqrt{t})} \right)^2 \quad (16)$$

where M_t is the mass of carbon dioxide sorbed at time t , M_∞ is the amount sorbed at equilibrium, L is the sample thickness (the sample is exposed to the gas phase on one side only). The value of \bar{D} calculated through eq 16 corresponds to the value of the carbon dioxide mutual diffusivity, D , at a certain concentration value, which can be evaluated following the procedures reported in ref 28. Because the sample volume increased with the carbon dioxide concentration, for each sorption step test, the sample thickness to be used in the analysis of data was evaluated from the mixture volume as predicted by SL EOS, taking the arithmetic average of initial and final densities of the polymer-gas mixture.

The investigated pressure range was 0–6.5 MPa. Buoyancy correction was also performed on the basis of the carbon dioxide density and volumes of the sample (as evaluated from SL EOS), pan, and spring. Volumes of the pan and spring were determined by evaluating the buoyancy effect at test conditions but without the polymer sample. An example of sorption kinetics is reported in Figure 1, where the normalized sorbed mass (M_t/M_∞) is plotted as a function of the square root of time. The sorption kinetics follow a Fickian behavior.²⁹

Sorption isotherms have been evaluated at each temperature and reported as equilibrium sorbed values versus pressure.

Density Measurements at Atmospheric Conditions. Because dilatometric experiments supplied the

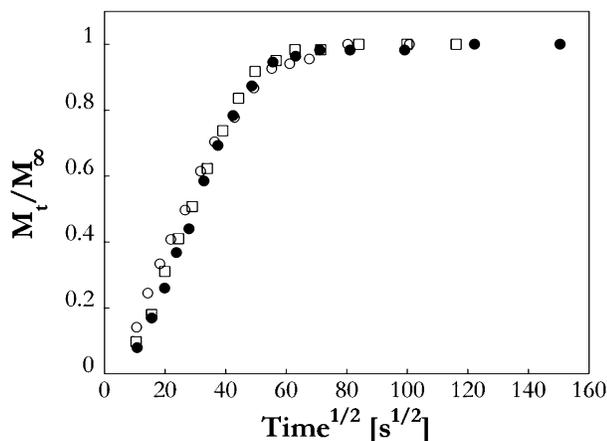


Figure 1. Experimental sorption kinetics for the PCL–CO₂ system at 70 °C: ○, 3.77 MPa; ●, 4.28 MPa; □, 4.81 MPa.

specific volume changes and not the absolute specific volume, one independent density measurement at 25 °C and at atmospheric pressure was necessary to evaluate absolute *PVT* data. The measurement was conducted by using the flotation technique. The sample was immersed in a water–NaCl solution at 25 °C, and the salt concentration was changed until flotation of polymer pellets. The density of the solution, and hence of the polymer, was then determined by using a hydrostatic balance.

Calorimetric Analysis. DSC analysis was performed to determine T_g and T_m of the polymer. A TA Instruments 2920 DSC was used in the temperature range –100 to +120 °C at a scanning rate equal to 10 °C/min, typically on a 10 mg sample. DSC was also used to determine the degree of crystallinity of the starting samples on the basis of the latent heat of melting (ΔH_m). An average value of $\Delta H_m = 43$ J/g was measured, which, when compared to the value of the latent heat of melting for an ideal PCL crystal ($\Delta H_m^0 = 76.6$ J/g³⁰), indicated a degree of crystallinity (X_c) equal to 0.57.

Results and Discussion

***PVT* Properties of PCL.** *PVT* data for pure PCL from isothermal experiments, at temperatures from 25 to 120 °C and pressures up to 200 MPa, are reported in Figure 2. The density of PCL at room temperature and pressure, as measured with the flotation method, was equal to 1.140 g/cm³.

Parameters of SL and Tait EOSs for PCL were evaluated from *PVT* data in the melt region, at temperatures higher than 65 °C. The results are synthesized in Table 1.

PVT data for PCL evaluated in this work are in good agreement with the values of SL EOS parameters predicted theoretically by molecular dynamics simulations.³¹

CO₂ Sorption Isotherms in Molten PCL. Figure 3 shows the experimental sorption isotherms of CO₂ in PCL. As expected, the equilibrium concentration increases with the pressure and decreases with the temperature.

The experimental data were fitted with the SL model for the mixture by using for pure PCL the SL EOS parameters obtained experimentally in the range of 0–50 MPa (Table 1) and for carbon dioxide the SL EOS parameters as taken from the literature,^{6,7} i.e., $P^* = 5670$ atm, $T^* = 305$ K, and $\rho^* = 1.51$ g/cm³. A good

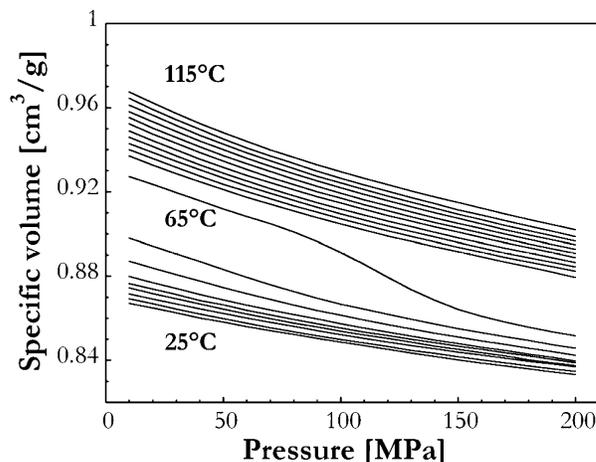


Figure 2. Isothermal experimental *PVT* data for PCL in the temperature range of 25–115 °C and in the pressure range of 0–200 MPa.

Table 1. Values of Parameters for Tait Equation and SL-EOS for PCL^a

	Tait	SL
up to 50 MPa	$B_0 = 2.3825 \times 10^2$ $B_1 = -3.9720 \times 10^{-3}$ $A_0 = 0.9487$ $A_1 = -1.0688 \times 10^{-3}$ $A_2 = 1.8983 \times 10^{-5}$ $A_3 = -6.8972 \times 10^{-8}$	$P^* = 548.6$ $V^* = 0.8635$ $T^* = 637.7$ $\sigma = 0.0001$ $\alpha = 0.0004$
up to 100 MPa	$B_0 = 2.3525 \times 10^2$ $B_1 = -3.7914 \times 10^{-3}$ $A_0 = 0.9487$ $A_1 = -1.0688 \times 10^{-3}$ $A_2 = 1.8983 \times 10^{-5}$ $A_3 = -6.8972 \times 10^{-8}$	$P^* = 558.1$ $V^* = 0.8572$ $T^* = 619.6$ $\sigma = 0.0001$ $\alpha = 0.0007$
up to 200 MPa	$B_0 = 2.3494 \times 10^2$ $B_1 = -3.5763 \times 10^{-3}$ $A_0 = 0.9487$ $A_1 = -1.0688 \times 10^{-3}$ $A_2 = 1.8983 \times 10^{-5}$ $A_3 = -6.8972 \times 10^{-8}$	$P^* = 611.6$ $V^* = 0.8440$ $T^* = 585.3$ $\sigma = 0.0001$ $\alpha = 0.0013$

^a Pressures are in MPa, volumes are in cm³/g, temperatures are in K, and deviations are in cm³/g. σ is the root mean square average deviation, while α is the average absolute deviation of the predicted volumetric data as compared to experimental data.

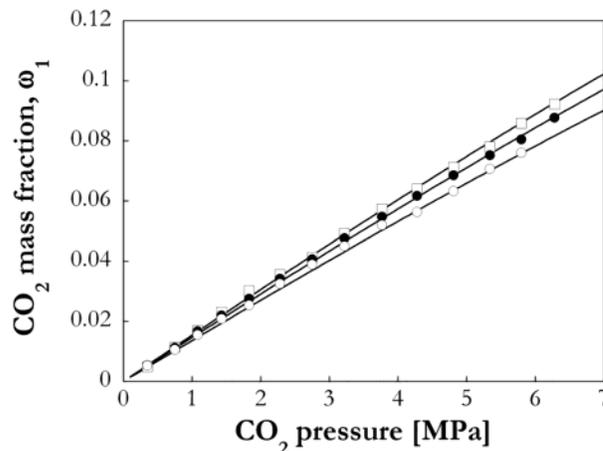


Figure 3. Sorption isotherms for the PCL–CO₂ system. Experimental data and isotherms predicted by SL EOS (continuous lines) using ψ as the fitting parameter: □, 70 °C; ●, 75 °C; ○, 85 °C.

agreement between theoretical prediction and experimental data was obtained by using ψ as a fitting parameter. The best fitting values for ψ increased only

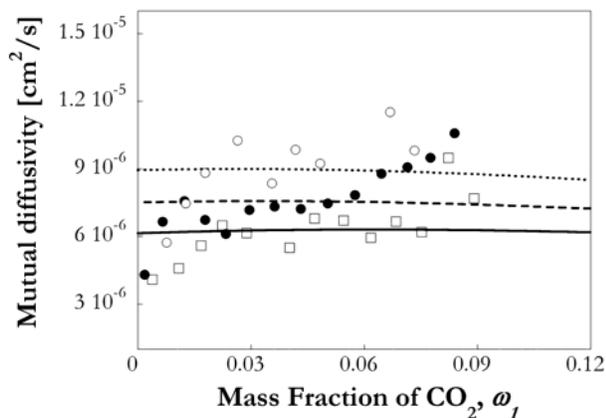


Figure 4. Mutual diffusivity for the PCL–CO₂ system. Experimental data and best-fitting curves calculated through eq 11 (see Table 2 for the values of the fitting parameters): □, 70 °C; ●, 75 °C; ○, 85 °C.

slightly with temperature, passing from 0.978 at 70 °C to 0.985 at 85 °C.

Evaluation of CO₂ Mutual Diffusivities. In Figure 4 are reported the mutual diffusivity data for the CO₂–PCL system at 70, 75, and 85 °C and at pressures ranging from 0 to 6.5 MPa, as a function of the penetrant weight fraction. In view of the relatively small weight fractions of carbon dioxide, eq 11 is well suited to fit experimental data for mutual diffusivity. Effects of carbon dioxide concentration, of pressure, and of temperature were all taken into account to evaluate $\hat{V}_{FH,M}$ from the SL EOS, as illustrated in the following.

To use eq 11, the values of \hat{V}_i^* , ξ , and $\hat{V}_{FH,M}$ needed to be evaluated first. In the following are illustrated the related calculation procedures.

Following Vrentas et al.,⁸ \hat{V}_1^* and \hat{V}_2^* were estimated by assuming them to be equal respectively to the specific volumes of the solvent and polymer at absolute zero temperature [i.e., $\hat{V}_1^* = \hat{V}_1^0(0)$ and $\hat{V}_2^* = \hat{V}_2^0(0)$]. In turn, specific volumes at 0 K were estimated using group contribution methods summarized by Haward³² and as described by Zielinski and Duda.³³ The values calculated using this procedure were $\hat{V}_{PCL}^* = 0.7491$ cm³/g and $\hat{V}_{CO_2}^* = 0.2932$ cm³/g.

It is worth noting that, according to Bondi,³⁴ an alternative route to evaluate volumes at 0 K could be, to a good approximation, the one based on the knowledge of the corresponding van der Waals volumes and packing density ratio at 0 K (the ratio of the van der Waals volume and the volume at 0 K). In the case of polymers, the following expression has been proposed:³⁴

$$\frac{\tilde{V}_{0,2}}{\tilde{V}_{W,2}} = \frac{\tilde{V}_{C,2}(0)}{\tilde{V}_{W,2}} \cong 1.3$$

where $\tilde{V}_{0,2}$, $\tilde{V}_{W,2}$, and $\tilde{V}_{C,2}(0)$ are respectively the 0 K equilibrium liquid molar volume, the van der Waals molar volume, and the 0 K crystalline molar volume, while the average packing density ratio is assumed to be 1/1.3. For both polymer and penetrant, the van der Waals volume can be estimated by using the group contribution method proposed by Bondi.^{34,35}

The parameter ξ was calculated to be equal to 0.2821 by estimating the molar volume of the polymer jumping subunit through the following equation introduced by

Zielinski and Duda:³³

$$\tilde{V}_{2J} = 0.6224 T_{g2} - 86.95 \quad (17)$$

and by assuming that the jumping subunit of carbon dioxide is the entire molecule (i.e., $M_{1J} = M_1$).

$\hat{V}_{FH,M}$ was evaluated through the following equation:

$$\hat{V}_{FH,M}(T) = \hat{V}_M(T) - (\hat{V}_{FI}(T) + \hat{V}_{0,M}) = \hat{V}_M(T) - [(\hat{V}_{FI,1}(T) + \hat{V}_{0,1})\omega_1 + (\hat{V}_{FI,2}(T) + \hat{V}_{0,2})\omega_2] \quad (18)$$

$\hat{V}_{FI,M}$ and $\hat{V}_{FI,i}$ represent the so-called *interstitial free volumes*²⁶ respectively of the mixture and of the pure components (the *interstitial free volume* is associated with anharmonic vibrations and is assumed to be uniformly distributed throughout the material: it is permanently located in the proximity of a molecule or a molecular segment and has a high redistribution energy).

$\hat{V}_{0,M}$ and $\hat{V}_{0,i}$ represent the so-called *specific occupied volumes*²⁶ respectively of the mixture and of the pure components.

The relevant assumption was made here that the sum of the occupied volume at 0 K and the interstitial free volume, for a pure substance, can be taken to be equal to the specific volume of the pure crystal, $\hat{V}_{C,i}$ [i.e., $(\hat{V}_{FI} + \hat{V}_{0,i}) \cong \hat{V}_{C,i}$]. This procedure was preferred to the one proposed by Zielinski and Duda,³³ which is quite complicated and involves the use of several unknown parameters.

Further, assuming volume additivity,⁸ the value of $\hat{V}_{FI} + \hat{V}_0$ for the mixture can be evaluated as

$$(\hat{V}_{FI} + \hat{V}_0)_M \cong \hat{V}_{C,1}\omega_1 + \hat{V}_{C,2}\omega_2 = \hat{V}_{C,M} \quad (19)$$

It was, then, possible to calculate the hole free volume of the mixture as $\hat{V}_{FH,M} = \hat{V}_M - (\hat{V}_{FI} + \hat{V}_0)_M$ once \hat{V} , $\hat{V}_{C,1}$, and $\hat{V}_{C,2}$ were known. At the temperature of interest, the CO₂ crystal is not thermodynamically stable and, consequently, its specific volume is not experimentally accessible. For this reason the specific volume of the CO₂ crystal ($\hat{V}_{C,1}$) has been evaluated by extrapolating data from the literature, which are available up to about 200 K.³⁶

Also the PCL crystal is not thermodynamically stable at temperatures of interest; hence, the specific volume of the PCL crystal ($\hat{V}_{C,2}$) was evaluated by extrapolating the values available below the melting temperature. To this aim, the values of $\hat{V}_{C,2}$ below T_m have been calculated from the following equation:

$$\hat{V}_{C,2}(T) = \frac{\hat{V}_{SC,2}(T) - \hat{V}_{A,2}(T)(1 - X_c)}{X_c}, \quad \text{at } T < T_m \quad (20)$$

where the specific volume of the semicrystalline sample ($\hat{V}_{SC,2}$) has been measured from dilatometric experiments, while the specific volume of the amorphous PCL ($\hat{V}_{A,2}$) at $T < T_m$ was evaluated by extrapolating experimental dilatometric data obtained at higher temperatures. X_c , which represents the crystalline fraction of the starting sample, has been evaluated from DSC to be equal to 0.57 (see the Experimental Section on DSC). Finally, the crystal specific volume ($\hat{V}_{C,2}$) at temperatures of interest was evaluated by extrapolating data calculated at $T < T_m$. The procedure is summarized in Figure 5.

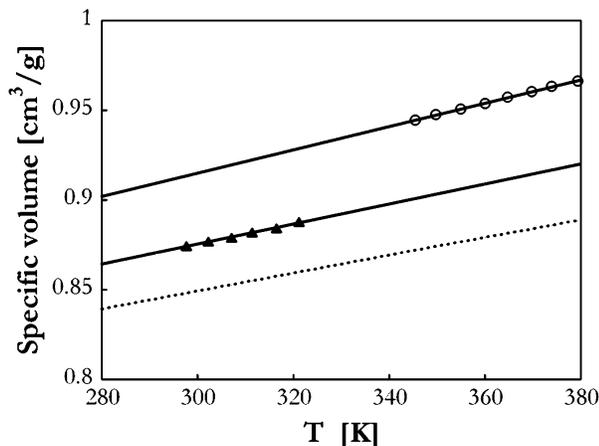


Figure 5. Evaluation procedure of the hypothetical specific volume of the PCL crystal at $T > T_m$: \circ , amorphous PCL (PVT data); \blacktriangle , semicrystalline PCL (PVT data); dotted line, crystalline PCL (value predicted through eq 20 using $X_c = 0.57$).

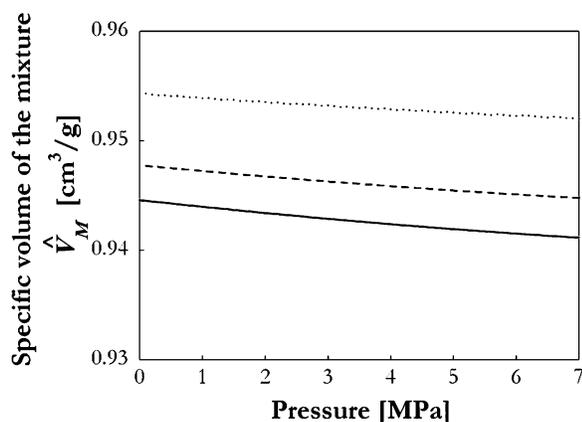


Figure 6. Specific volumes of the mixture, as predicted by SL EOS: solid line, 70 °C; dashed line, 75 °C; dotted line, 85 °C.

$(\hat{V}_{FI} + \hat{V}_0)_M$ as a function of the carbon dioxide mass fraction at 70, 75, and 85 °C was then evaluated from eq 19 by using the calculated values of $\hat{V}_{C,1}$ and $\hat{V}_{C,2}$ and assuming that $(\hat{V}_{FI} + \hat{V}_0)_i$, in the investigated range, is not dependent on the pressure.

The specific volume of the mixture, which is also needed in eq 18, has been calculated as

$$\hat{V}_M = 1/\bar{\rho}\rho^* \quad (21)$$

Figure 6 shows the results in terms of the specific volume of the mixture as a function of the pressure at the three investigated temperatures.

The $\hat{V}_{FH,M}$ values were finally calculated through eq 18 and are reported in Figure 7. These values were used in eq 11 to evaluate mutual diffusivities of CO_2 and PCL. In eq 11, D_{01} and γ were used as fitting parameters for data measured at 70 °C. Then, fitting of the data at 75 and 85 °C was performed by keeping constant D_{01} , equal to the value calculated at 70 °C, and using γ as the only fitting parameter. Values of the fitting parameters are summarized in Table 2, and curve-fitting results are reported in Figure 4. As expected for the case of small molecules, mutual diffusivity is a weak function of the concentration. Similar behavior has been reported in the recent literature for the case of carbon dioxide diffusion in other molten biodegradable polymers.³⁷ In general, the dependence of the diffusion coefficient on the concentration increases as the size of the penetrant

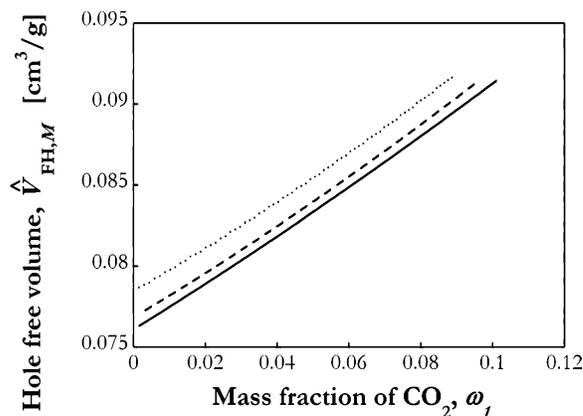


Figure 7. Specific hole free volume of the PCL– CO_2 mixture, as calculated through eq 18: solid line, 70 °C; dashed line, 75 °C; dotted line, 85 °C.

Table 2. Best-Fitting Values for D_{01} and γ Obtained by Fitting of the Experimental Mutual Diffusivity Data for the CO_2 –PCL System with Equation 11

test temp (°C)	D_{01} (cm ² /s)	γ
70	$1 \times 10^{-4} \pm 2 \times 10^{-5}$	0.97 ± 0.03
75	$1 \times 10^{-4} \pm 2 \times 10^{-5}$	0.87 ± 0.03
85	$1 \times 10^{-4} \pm 2 \times 10^{-5}$	0.85 ± 0.03

increases. In fact, the higher the molecular weight of the penetrant is, the smaller the number of molecules for the same mass fraction and the higher the average hole free volume per molecule.⁸

Conclusion

The system molten PCL–carbon dioxide has been analyzed to characterize solution thermodynamics and mutual diffusivity. Sorption experiments have been performed on molten PCL, and equilibrium data have been successfully correlated by means of the SL theory using the interaction parameter ψ to best fit the data.

Mutual diffusivity values, as determined from sorption kinetics assuming ideal Fickian behavior, have been shown to depend only weakly on the carbon dioxide concentration and pressure. The Duda and Vrentas free-volume theory has been used to interpret diffusivity data, and the *hole free volume* of the polymer–gas mixture, needed for the evaluation of self-diffusivity, has been evaluated from solution thermodynamics.

These results were used to tailor the foaming process of PCL by using carbon dioxide as a foaming agent. A good control of the foam structure was possible, as will be illustrated in a forthcoming contribution.

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