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In Situ IR Spectroscopy and Ab Initio Calculations To Study Polymer Swelling by Supercritical CO₂

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The CO₂ sorption and polymer swelling of hydroxytelechelic polybutadiene (HTPB) and poly(ethylene glycol) (PEG) have been investigated as a function of temperature and CO₂ pressure by combining in situ near-infrared spectroscopy with molecular modeling. The results reported here for the PEG–CO₂ system are in a very good agreement with literature data hence validating our experimental procedure. It has been found that CO₂ sorption and swelling effect is more important for PEG than for HTPB. For both polymers, an increase of temperature leads to a strong decrease of both the CO₂ sorption and swelling. In order to identify at a molecular level the nature and strength of intermolecular interaction occurring between CO₂ and the polymers, ab initio calculations have been performed on model structures, representative of the main functional group of the polymer, and their complex with CO₂. Trans-3-hexene (3-Hex), propyl methyl ether (PME) and methoxytrimethylsilane (MTMS) have been selected to mimic the functional groups of HTPB, PEG and polydimethyl siloxane (PDMS), respectively. The last system has been chosen since previous works on the swelling of PDMS by high pressure CO₂ have revealed the high ability of CO₂ to swell both uncrosslinked and crosslinked PDMS. The calculated stabilization energies of the MTMS–CO₂, PME–CO₂, and 3-Hex–CO₂ dimers indicate that CO₂ interacts specifically with the three moieties through a Lewis acid–Lewis base type of interaction with the energies displaying the following order: E(MTMS–CO₂) = –3.59 > E(PME–CO₂) = –3.43 > E(3-Hex–CO₂) = –2.5 kcal/mol. Since the solubility of CO₂ in the corresponding homopolymers follows the same order, it is evidenced that the stronger the interaction between CO₂ and the polymer, the higher the CO₂ sorption. Therefore, even if one cannot exclude the influence of free volume and chain flexibility of the polymer, it appears that the solubility of CO₂ in the polymer is predominantly governed by the interaction between CO₂ and the polymer. Although the same trend is observed for the swelling of the polymer as a function of the CO₂ pressure, we have found that for a given value of CO₂ sorption, the swelling of the polymer depends on its nature, meaning that the swelling is not only governed by the CO₂–polymer interaction but also by other intrinsic properties of the polymer.

1. Introduction

The use of supercritical carbon dioxide (scCO₂) as a substituent to harmful solvent systems for both chemical syntheses and polymer processing has been the subject of a particular attention in the last years.^{1–7} Indeed, its critical coordinates are easily accessible ($T_c = 31\text{ }^\circ\text{C}$, $p_c = 7.38\text{ MPa}$, $\rho_c = 0.468\text{ g}\cdot\text{cm}^{-3}$), and CO₂ is nonpoisonous, nonflammable, chemically inert, inexpensive, and easily available. In addition, scCO₂ exhibits a good solubility in a number of polymers; increasing the CO₂ pressure induces a significant increase of the initial volume of the polymer (swelling) and

modifies its morphological and functional properties. In other words, the addition of small amounts of compressed CO₂ to the polymer phase results in substantial changes of its physical properties such as its viscosity, permeability, interfacial tension, and glass transition temperature. Thus, carbon dioxide can be used as a temporary plasticizer, facilitating the absorption of additives into polymers. Another great advantage of scCO₂ compared to traditional organic solvents is that it leaves quickly the polymer during the depressurization of the system, without any solvent residue. Consequently, the stage of drying, necessary when using a liquid solvent, is nonexistent here. This polymer processing method has found a large number of applications in various fields such as particle formation, foaming, and blending as well as impregnation of active chemical species that have been recently reviewed in the literature.^{2,3,8} Therefore, understanding the mechanisms underlying the CO₂ solubility and diffusivity in polymers, as well as their subsequent swelling in all these processes is of great importance as they

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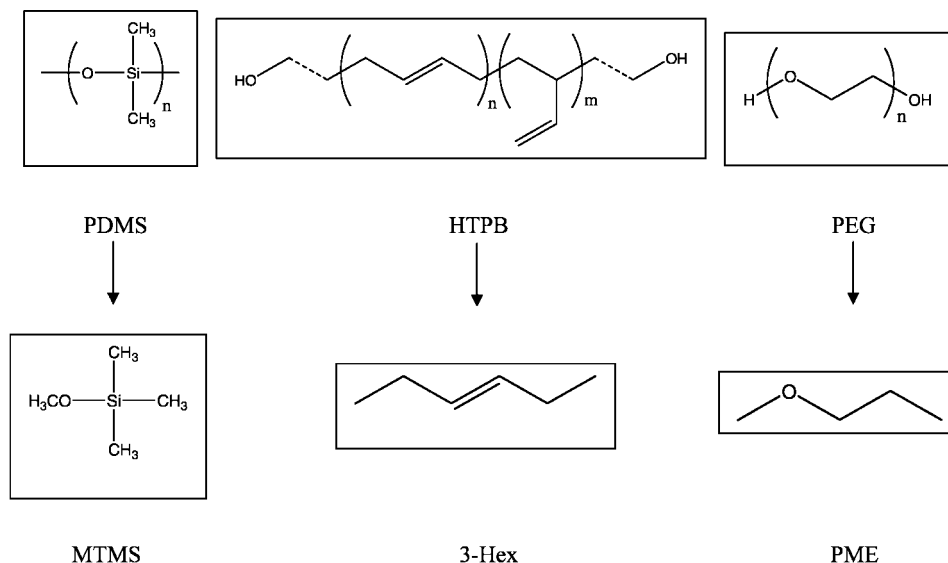


Figure 1. Structures of the polymers and their corresponding model structures.

are expected to provide a wide range of opportunities in polymer processing for the plastics industry.

A large variety of polymers have already been investigated such as poly(ethylene glycol) PEG, polydimethyl siloxane (PDMS), poly(methyl methacrylate) PMMA, polystyrene (PS), polycarbonate (PC), polyethylene terephthalate (PET).^{9–14} Some reviews^{2,3} present good literature data surveys on CO₂–polymers systems, showing that the solubility of scCO₂ in a polymer can be either negligible or reach a weight percentage of about 40%, depending on its nature. To get such CO₂ sorption data, various methods have been developed such as the barometric, gravimetric, and the frequency modulation methods.² More recently, spectroscopy techniques such as attenuated total reflection-infrared (ATR-IR)^{15–17} and near-infrared (NIR) transmission spectroscopy¹⁸ have proven very effective in the simultaneous measurement of CO₂ sorption and polymer swelling, according to the CO₂ pressure, for many polymers.

Although it is not easy to rationalize the current state of the art on the understanding of the polymer–CO₂ phase behavior, it is now generally admitted that the affinity of CO₂ for a polymer is mainly related to intermolecular interactions occurring between CO₂ and the polymer, even if in some cases the chain flexibility as well as the free volume of the polymer has a greater effect on the solubility than the gas–polymer interactions.¹⁹ These specific intermolecular forces and their relationship with CO₂ sorption were investigated qualitatively by few authors using FTIR spectroscopy.^{20,21} However, no quantitative relationship between the nature and the strength of the interactions between the polymer and CO₂ and its ability to swell the polymer has been reported at this point. Indeed, to the best of our knowledge, the molecular origin of the ability of CO₂ to swell a polymer has only been little investigated in detail for fluoropolymers²² and polyethylene²³ using molecular modeling methods. In particular, the work on polymer–gas mixtures reported by van der Vegt²³ was aimed to determine quantities like solvation Gibbs energies, enthalpies, and entropies using molecular dynamics simulations, as well as the contributions of polymer reorganization and penetrant binding to the solvation enthalpy (the interactions among the dissolved penetrants may be ignored). Thus, in the solvation process, there is a competition between the work required to create a cavity in the polymer (that implies a polymer reorganization) and the binding energy between the solute and the polymer. For weak interacting gases

like He, Ne, and H₂, the energy associated with the polymer reorganization processes dominates over the solute binding interaction with the polymer, rendering positive values of the solvation enthalpy. However, an opposite behavior was found for CO₂, where the solute binding interaction was found to be predominant.

These considerations prompt us to investigate at the molecular level how far the sorption of high-pressure CO₂ in model polymers is correlated to the nature and strength of the CO₂–polymer interaction. In this purpose, we have chosen to investigate three different polymers, namely PDMS, PEG, and hydroxytelechelic polybutadiene (HTPB) (Figure 1). The choice of these model systems was driven by our wish to study different homopolymers that can be more or less swollen by scCO₂. First, previous studies concerning the swelling of PDMS by high pressure CO₂ have revealed the high ability of CO₂ to swell both uncrosslinked and crosslinked PDMS. Swelling values of PDMS by CO₂ as high as 60% at 50 °C and 10 MPa have been reported.^{11,16} The second polymer, PEG, can be considered as an intermediate system as it can be swollen by CO₂ by up to 25% at 40 °C and 10 MPa.^{10,24} Finally, we have studied HTPB, which is expected to have a lower swelling rate. Although PEG has already been the subject of numerous investigations, it has been considered in this study as a validation system for our experimental procedure, which has been further applied to determine the swelling and CO₂ sorption of HTPB. Finally, literature data concerning PDMS have been compared to our results obtained for PEG and HTPB. In this work, we have chosen to use *in situ* NIR transmission spectroscopy for a quantitative determination of the CO₂ sorption and swelling of PEG and HTPB in scCO₂. Performing transmission spectroscopy in the spectral range 4000–10 000 cm^{−1} has some advantages over the traditional mid-infrared spectroscopy, as previously shown by Guadagno et al.¹⁸ In particular, molar absorption coefficients of combination bands are expected to exhibit little sensitivity upon temperature and pressure conditions,^{25,26} which is not the case for fundamentals. For example, Buback et al.²⁷ have shown that the molar absorption coefficient of combination bands of CO₂ were almost independent of the CO₂ density. Therefore, this spectral region has been often used for concentration measurements. Besides, the use of *in situ* NIR spectroscopy makes it possible to detect impurities that could be present

in the polymer, inducing potentially a non-negligible effect on the swelling of the polymer.

Meanwhile, *ab initio* calculations have been performed in order to obtain information on the nature of the polymer–CO₂ intermolecular interactions. Although statistical mechanical simulations are well adapted to get insights of the phase behavior of polymer–gas mixtures, *ab initio* calculations are preferred in order to compute accurate interaction energies. The calculations have been performed on model structures that are representative of the main functional groups of the backbone of PDMS, PEG, and HTPB (Figure 1). The equilibrium geometries of these model structures and their complexes with CO₂, in particular, on methoxytrimethylsilane (MTMS), propyl methyl ether (PME), and trans-3-hexene (3-Hex), representative of PDMS, PEG, and HTPB, respectively, have been investigated. Note that such an approach does not take into account neither the polymer–polymer interaction, the CO₂–CO₂ interaction nor the solvent accessible surface area²⁸ of CO₂ in connection with the free volume of the polymer. However, it was previously reported^{22,23,28} that in the case of CO₂, these effects may be less relevant than the CO₂–polymer interactions. Therefore, we have decided to use such accurate method in order to rationalize the relation between the nature and strength of the polymer–CO₂ interaction and the concentration of CO₂ that can be incorporated into the polymer.

2. Experimental Section

2.1. Chemicals. PEG (Mw = 400 g/mol) was purchased from Sigma. Hydroxytelechelic polybutadiene or HTPB R45 HT (Mn = 2600 g/mol) was provided by Arkema. Structures of the polymers are displayed in Figure 1. Carbon dioxide N45 (purity 99.95%) was supplied by Air Liquide.

2.2. Infrared Setup. The infrared absorption measurements were performed on a Biorad interferometer (type FTS-60A) equipped with a dual source capability (a globar and a tungsten halogen source), two different beamsplitters (a KBr/Ge and a quartz plate) and a DTGS (deuterated triglycine sulfate) detector in order to investigate the spectral ranges (400–6500 cm^{−1}) and (3000–11500 cm^{−1}), respectively. Single beam spectra recorded with a 2 cm^{−1} resolution were obtained after the Fourier transformation of 50 accumulated interferograms.

The near-infrared absorption experiments were performed using a homemade stainless steel cell²⁹ equipped with four cylindrical sapphire windows with a path length of 6.7 mm. The sealing was obtained using the unsupported area principle. The windows were positioned on the surface of a stainless plug, while a 100 μm Kapton foil placed between the window and the plug compensated for any imperfections between the two surfaces. Teflon O-rings were used to ensure the sealing between the plug and the cell body. The cell was heated using cartridge heaters disposed in the periphery of the body of the cell. Two thermocouples were used, the first one located close to a cartridge heater for the temperature regulation and the second one close to the sample area to measure the temperature of the sample with an accuracy of about 2 °C. The cell was connected via a stainless steel capillary to a hydraulic pressurizing system that allows the pressure to be raised up to 50 MPa with an absolute uncertainty of ±0.1 MPa and a relative error of ±0.3%. The stabilization of the operating conditions was controlled by recording several consecutive spectra.

2.3. Experimental Procedure. The cell was first filled with the polymer, then pumped under vacuum in order to remove any trace of water in the polymer and finally heated up to the required temperature. The spectra were recorded for the raw

polymer, then CO₂ was added up to the highest desired pressure. The system was kept under isobaric and isothermal conditions for a long period of time (typically from a few hours at high temperature up to 2–3 days at 40 °C) in order to ensure that the equilibrium was achieved. After recording the spectrum, the pressure was decreased to a lower value. For each pressure, the equilibrium was considered to be achieved when no change of the spectral bands was noticed.

3. Computational Details

Calculations were performed on three model structures, namely MTMS, PME, and 3-Hex, selected to mimic the functional groups of PDMS, PEG and HTPB, respectively (Figure 1). The initial configuration used for MTMS,³⁰ PME,³¹ and 3-Hex³² was the lowest energy conformer previously reported by authors who investigated the conformational properties of these molecules using *ab initio* and density functional theory (DFT) calculations. Preliminary geometry optimizations were carried out using a semi empirical model (AM1³³) to determine the most stable conformations of the MTMS–CO₂, PME–CO₂ and 3-Hex–CO₂ adducts. These semiempirical calculations were carried out using the AMPAC software.³⁴ The lowest energy adducts obtained at the AM1 level were further investigated using an *ab initio* method implemented in the Gaussian 2003 package.³⁵ Calculations of geometries and energies reported in this paper were carried out at the second-order Moller–Plesset level (MP2), which includes explicitly the effects of electron correlation.³⁶ The augmented correlation-consistent polarized valence double basis sets (aug-cc-pVDZ) proposed by Dunning and co-workers were used in these calculations.^{37–40} Geometry computations were not subjected to a particular symmetry constraint, excepted for isolated CO₂ (*D_{∞h}* symmetry). Stabilization energies of the adducts investigated in this paper were calculated using the “supermolecule” method as the difference in energy between each adduct and the sum of the isolated monomers. The basis set superposition errors (BSSE) were calculated using the full counter-poise method of Boys and Bernardi.⁴¹ Molden was used to display the optimized geometry of the isolated moieties and the complex.⁴²

4. Results and Discussion

4.1. Near-Infrared Absorption Spectra. The infrared spectra of HTPB subjected to CO₂ were recorded for pressures up to 25 MPa and for three different temperatures: 40, 100, and 150 °C. Figure 2a illustrates the spectral changes in the wavenumber range 4400–6200 cm^{−1} that occur with an increasing CO₂ pressure. A number of significant peaks associated to combination or overtones of the polymer can be observed in the spectral range 4400–4800 and 5500–6200 cm^{−1}. Increasing the CO₂ pressure leads to a decrease of the intensities of the polymer bands (for example at 4720 and 6105 cm^{−1}), whereas the intensity of the CO₂ peaks, characteristic of CO₂ sorbed into the polymer (for example at 4950 cm^{−1}), increases. Note that the three more intense peaks observed in Figure 2a (centered at 4480, 5660, and 5820 cm^{−1}) are saturated in our experimental conditions and cannot be used for our purpose. Besides, the peaks centered at 4600, 4660, 4720 strongly overlap, making it difficult to extract accurate quantitative information from these contributions. Consequently, we have used the peak centered at 6105 cm^{−1} to determine the swelling of HTPB subjected to scCO₂. Concerning CO₂, we can detect two peaks at 4950 and 5100 cm^{−1} that are assigned to the combination modes $\nu_1 + 2\nu_2 + \nu_3$ and $2\nu_1 + \nu_3$ of the CO₂

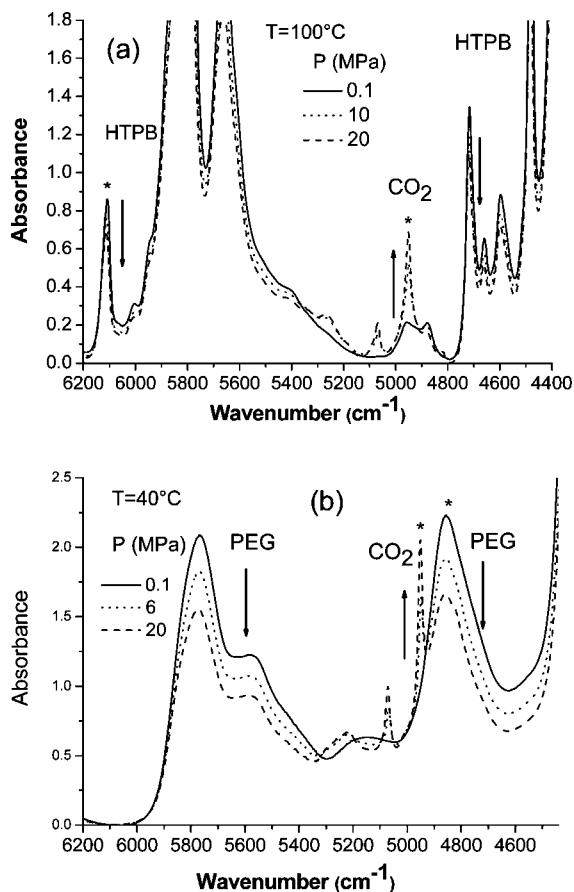


Figure 2. IR absorption spectra of HTPB (a) and PEG (b) at different pressures of scCO₂ and constant temperature. The arrows indicate the intensity variation upon increasing the pressure. The asterisks show the peaks used for the determination of the CO₂ sorption and the polymer swelling.

molecule, respectively.⁴³ Because of the weak intensity of the peak at 5100 cm⁻¹, we have used the band at 4950 cm⁻¹ to estimate the evolution of the weight percentage of CO₂ incorporated into the polymer as a function of the CO₂ pressure. The near-infrared spectra of PEG 400 subjected to CO₂ was recorded the same way for pressures up to 20 MPa and for two different temperatures, 40 and 150 °C (see Figure 2b). In this case, we have used the peak centered at 4850 cm⁻¹ to determine the swelling of PEG, while using the band centered at 4950 cm⁻¹ to estimate the evolution of the weight percentage of CO₂ incorporated into the polymer.

4.2. Data Processing for the Determination of CO₂ Sorption and Polymer Swelling. *a. Polymer Swelling.* As previously proposed by Guadagno et al.,¹⁸ the polymer swelling can be calculated via the absorbance of a specific band of the polymer before and after exposure to CO₂, using the following procedure, according to the Beer–Lambert law:

$$A_0 = \varepsilon \cdot C_0 \cdot l \quad (1)$$

$$A = \varepsilon \cdot C \cdot l \quad (2)$$

Where A_0 , A , C_0 , and C are the absorbances of polymer bands and concentrations of polymer before and after exposure to CO₂, respectively, and l is the path length of the cell.

If V is the volume of the polymer before exposure to gas and $V + \Delta V$ is the volume of the polymer during exposure to gas, one can write

$$\frac{C_0}{C} = \frac{V + \Delta V}{V} = 1 + \frac{\Delta V}{V} = 1 + S \quad (3)$$

Finally, after combination of these three equations, the swelling S is given by

$$S = \frac{A_0}{A} - 1 \quad (4)$$

On the basis of the above considerations, we have selected the peak centered at 6105 cm⁻¹ to determine the swelling of HTPB.

The integrated areas A_0 and A of this band were calculated in the wavenumber range (6080–6170 cm⁻¹). In the case of PEG, we have used the peak centered at 4850 cm⁻¹. However, the swelling was determined from the variation of the maximum absorbance of this peak instead of its integrated area.

b. CO₂ Sorption. In order to determine the concentration of CO₂ (C_{CO_2}) incorporated into the polymer, we have applied the Beer–Lambert law using the integrated absorbance of the $\nu_1 + 2\nu_2 + \nu_3$ band of CO₂ centered at 4950 cm⁻¹ as follows

$$\int_{\nu'}^{\nu''} A(\nu) \cdot d(\nu) = \varepsilon \cdot C \cdot l \quad (5)$$

where ε is the molar absorption coefficient (L·mol⁻¹·cm⁻²) associated to the $\nu_1 + 2\nu_2 + \nu_3$ band of CO₂, C is the concentration of CO₂ (mol·L⁻¹), and l is the path length of the cell (cm). The wavenumber range considered for the integration of the $\nu_1 + 2\nu_2 + \nu_3$ band extends from 4880 (ν') to 5030 cm⁻¹ (ν''). The molar absorption coefficient was estimated in previous investigations²⁷ on pure CO₂ and was found to be constant over a wide range of density (up to 0.9 g·cm⁻³) and temperature (27 to 227 °C). Thus, the molar absorption coefficient of this peak was assumed to be the same when CO₂ swells the polymer and we have used for the considered wavenumber range a value of 10 L·mol⁻¹·cm⁻². For a straightforward comparison with the literature data, the weight percentage of CO₂ (% mass CO₂) sorbed into the polymer matrix was calculated using the following expression:¹⁸

$$\% \text{ mass CO}_2 = \frac{C_{CO_2}}{C_{CO_2} + \frac{\rho_{pol}}{1 + S}} \quad (6)$$

Where ρ_{pol} (mol·L⁻¹) represents the density of the polymer and S the swelling of the polymer after exposure to CO₂, obtained from the ratio $\Delta V/V$ (see above). Because of the presence of a weak peak of HTPB located at about 4960 cm⁻¹ (see Figure 2a), the spectrum of pure polymer at the considered temperature was subtracted for all registered spectra.

4.3. CO₂ sorption in HTPB and PEG. The weight percentage of sorbed CO₂ calculated using eqs 5 and 6 is reported in Figure 3 as a function of pressure at 40, 100, and 150 °C for HTPB and at 40 and 150 °C for PEG in Figure 4. For comparison, we have displayed in Figure 4 the results obtained by Guadagno et al.¹⁸ and Gourgouillon et al.¹⁰ for PEG 400 at

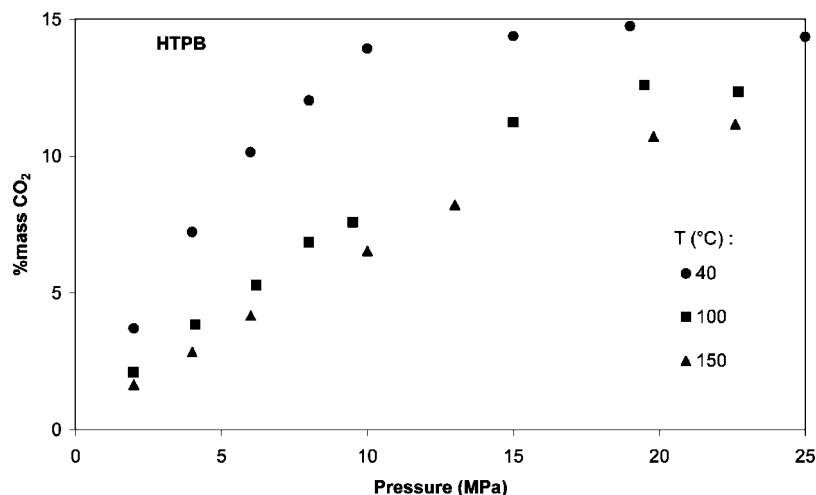


Figure 3. Weight percentage of CO₂ incorporated into polymer matrix of HTPB at 40 (●), 100 (■), and 150 °C (▲) as a function of the pressure of scCO₂.

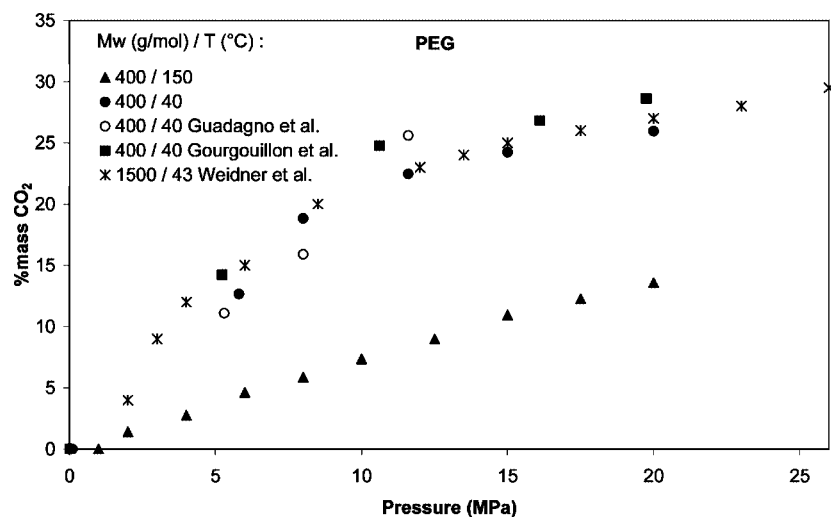


Figure 4. Comparison of weight percentage of CO₂ incorporated into polymer matrix of PEG at 40 (●) and 150 °C (▲) as a function of the pressure of scCO₂ with literature data.

40 °C and by Weidner et al.²⁴ for PEG 1500 at 43 °C. In the case of HTPB at 40 °C, the weight percentage of sorbed CO₂ increases with the pressure to reach a plateau-like value of about 15% at 10 MPa indicating that above this pressure, no more CO₂ can be incorporated into the polymer. A similar increase with a much less pronounced plateau-like behavior is observed for the measurements performed at higher temperatures (100 and 150 °C) but for a given pressure, an increase of temperature causes a decrease of the weight percentage of CO₂ incorporated into the polymer.

In the case of PEG, it appears clearly that the weight percentage of CO₂ sorbed, displaying the same plateau behavior as a function of CO₂ pressure, is higher than in HTPB and found to be about 20% at 10 MPa. Although small discrepancies are observed between the different sets of data, probably due to the different experimental and analytical methods employed, an overall good agreement is obtained between our data and that previously reported. Similarly to the case of HTPB, an increase of temperature causes a decrease of the weight percentage of CO₂ incorporated into the PEG, for a given pressure.

Thus, since the solubility of CO₂ is higher in PEG than in HTPB, CO₂–ether interactions are expected to be stronger than CO₂–double C=C bond interactions. The nature of the molecular interactions responsible for the differences in the solubility of

CO₂ into PEG and HTPB are investigated by means of quantum calculations in the Section 4.5.

4.4. Swelling of PEG and HTPB. The swelling of the polymer calculated using eq 4 is reported as a function of pressure at 40, 100, and 150 °C for HTPB in Figure 5 and at 40 and 150 °C for PEG in Figure 6. For comparison, we have displayed in Figure 6 the results obtained by Guadagno et al.¹⁸ for PEG 400 at 40 °C. In the case of HTPB at 40 °C, the swelling increases with the pressure up to a maximum value of about 15% reached for a pressure of 15 MPa, above which CO₂ cannot swell additionally the polymer. A similar behavior is observed for the measurements performed at higher temperatures (100 and 150 °C). However, for a given pressure an increase of temperature causes a decrease of the polymer swelling. Considering the PEG, the swelling increases with the pressure up to a value of about 35% reached at a pressure of 20 MPa. Similarly to HTPB, an increase of temperature for a given pressure causes a decrease of PEG swelling. Finally, according to the CO₂ sorption, the comparison of Figures 5 and 6 clearly shows that PEG swelling is higher than that measured for HTPB.

4.5. Analysis of the Polymer–CO₂ Interactions from Ab Initio Calculations: Structural and Energetic Considerations. In order to investigate at a molecular level how the solubility of CO₂ in PDMS, PEG, and HTPB is correlated to the nature

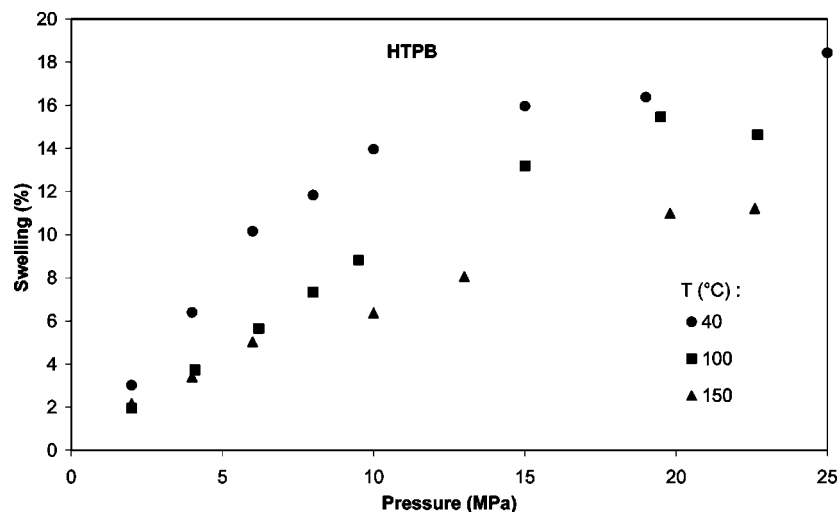


Figure 5. Swelling percentage of HTPB at 40 (●), 100 (■), and 150 °C (▲) as a function of the pressure of scCO₂.

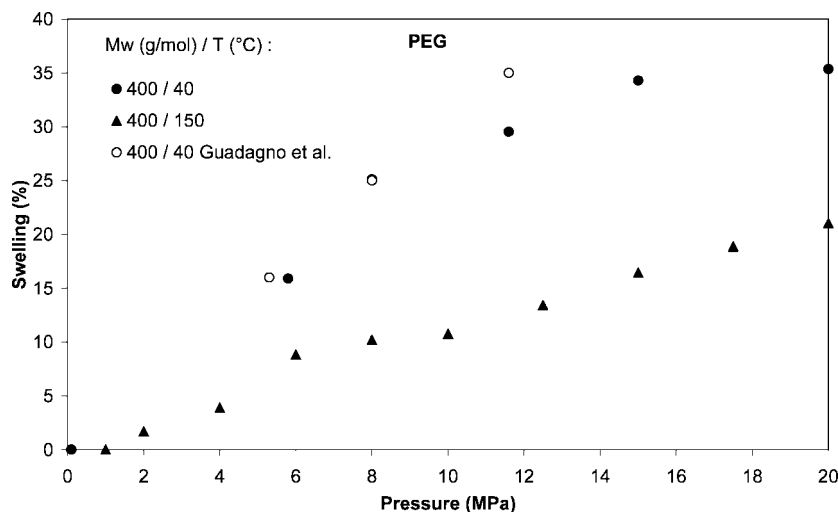


Figure 6. Comparison of swelling percentage of PEG at 40 (●) and 150 °C (▲) as a function of the pressure of scCO₂ with literature data.

and strength of the CO₂–polymer interaction, we have performed *ab initio* calculations on three model structures, namely MTMS, PME, and 3-Hex, chosen to mimic the functional groups of PDMS, PEG, and HTPB, respectively. Although these quantum chemistry methods do not allow modeling the entire polymer the way it could be done through statistical simulations, accurate interaction energies between CO₂ and the characteristic functional groups of polymers can be obtained. Let us emphasize that high level quantum mechanical methods (accounting for electron correlation effects) are required in order to compute accurate energies as the interactions in these systems are expected to be weak. Therefore, in order to calculate the geometry of the isolated PME–CO₂, MTMS–CO₂, and 3-Hex–CO₂ pairs, we have performed *ab initio* calculations at the second order Moller–Plesset perturbation theory (MP2) using Dunning’s aug-cc-pVDZ basis set. Figure 7 shows the optimized structures of the three dimers with the more relevant calculated structural parameters. Note that the initial configurations used for the PME, the 3-Hex, and the MTMS molecules, taken as the lowest energy conformers reported in previous studies, are almost unchanged upon complexation with CO₂. However, the isolated CO₂ molecule, which has a d_{coh} symmetry and a C=O bond length of 1.18022 Å, is systematically perturbed upon complexation, in particular concerning the O=C=O angle (cf. Figure 7).

In the case of PME–CO₂ dimer, CO₂ is found to be above the oxygen atom of PME for which the donating lone pair interacts with the carbon atom of CO₂. Such configuration reveals a Lewis Acid–Lewis Base (LA–LB) type of interaction where PME plays the role of a Lewis base and CO₂ the role of a Lewis acid. Such configuration is consistent with previous calculations performed on ether–CO₂ complex.^{44,45} The calculated binding energy of the complex, corrected for the BSSE, is found to be approximately –3.43 kcal/mol, which is in good agreement with that reported in the literature for the methyl butyl ether (MBE)–CO₂ complex⁴⁵ (–3.49 kcal/mol at the MP2/ aug-cc-pVTZ level). Such interaction energy is not negligible and evidence the good affinity of ether function with CO₂ as it has been found for polymer containing ether group.^{45–47}

Similarly to the PME–CO₂ adduct, CO₂ is found to be above the oxygen atom of MTMS in the MTMS–CO₂ dimer, which unveil a LA–LB type of interaction. However, the calculated binding energy corrected for the BSSE is found to be –3.59 kcal/mol, which is a value slightly higher than the one found for the PME–CO₂ complex. Therefore, this higher energy of interaction could account for the significantly higher solubility of CO₂ in PDMS¹⁶ than in PEG. Note that the solubility of CO₂ in PDMS has been found to be about 25% at 50 °C and 10 MPa.^{11,16}

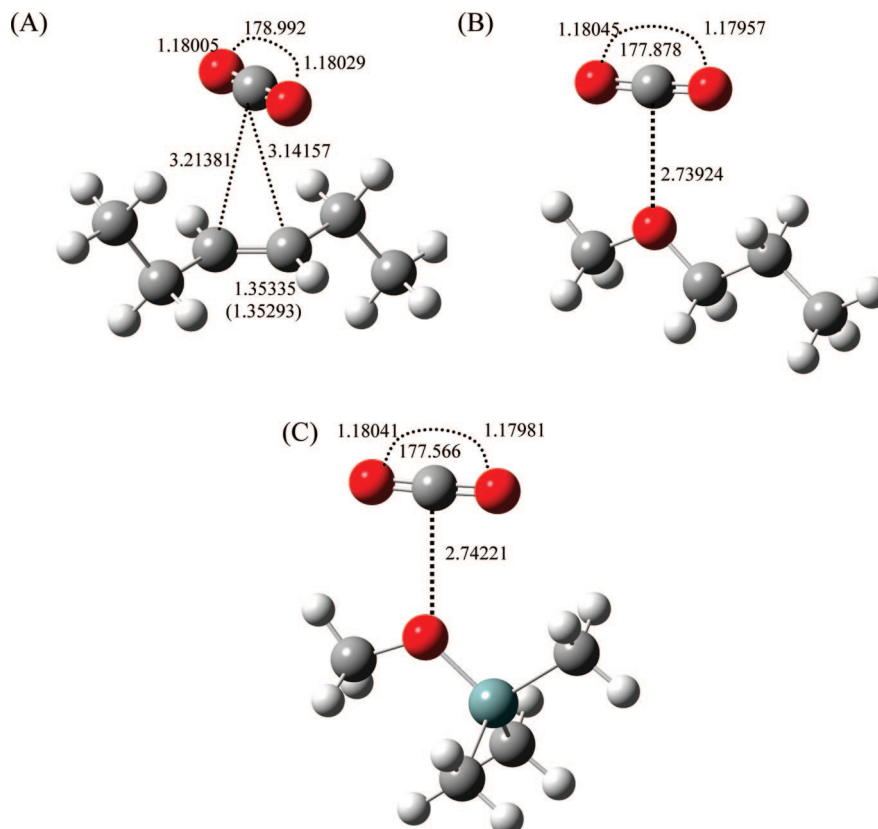


Figure 7. Optimized structure (MP2/aug-cc-pVDZ level) of the trans-3-hexene-CO₂ (A), propylmethylether-CO₂ (B), and the methyltrimethylsilane-CO₂ (C) dimer.

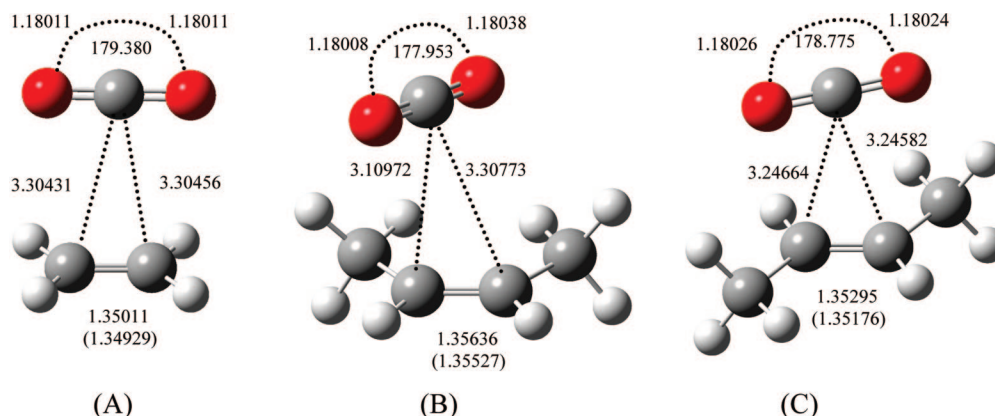


Figure 8. Optimized structure (MP2/aug-cc-pVDZ level) of the ethene-CO₂ (A), cis-dimethyl ethene-CO₂ (B) and trans-dimethyl ethene-CO₂ (C) dimer. Values in parentheses are reported for the molecule without CO₂.

Considering the 3-Hex-CO₂ dimer, the CO₂ molecule placed itself above the double bond of the 3-Hex molecule, the π electron of the C=C double bond interacting with the carbon atom of CO₂. The calculated binding energy of the complex, corrected for the BSSE is about -2.5 kcal/mol. This value is lower than the ones reported for both PME-CO₂ and MTMS-CO₂ complexes, which could a posteriori explain why the solubility of CO₂ in HTPB is lower than in PEG and PDMS.

In order to evaluate the influence of the model structure on the energy of interaction between CO₂ and a C=C double bond, we have performed the same calculations using ethene, trans-, and cis-dimethyl ethene as model structures of C=C double bond.

The optimized structures, calculated energies, and structural parameters are reported in Figure 8. The main features concerning the optimized structures are the same for all complexes:

CO₂ is found to placed itself above the C=C double bond, its main axis being almost parallel to the H-C=C-H plane, the angle between the main axis of CO₂ and the C=C bond depending on the model structure.

Concerning the ethene-CO₂ complex, the structure is found to be in agreement with previous reported calculations.⁴⁸ Also, the energy of interaction between CO₂ and ethene is found to be the lowest one of the series of ethene derivatives, about -1.5 kcal/mol. The calculated energies reported for the cis- and trans-dimethyl ethene are found to be almost the same (about -2.3 kcal/mol) and very close to the value calculated for the 3-Hex-CO₂ complex (-2.5 kcal/mol). Thus, whatever the model structure used to mimic the HTPB-CO₂ interactions, it appears that the interaction between CO₂ and a C=C double bond is lower than the LA-LB interaction occurring between CO₂ and an ether group.

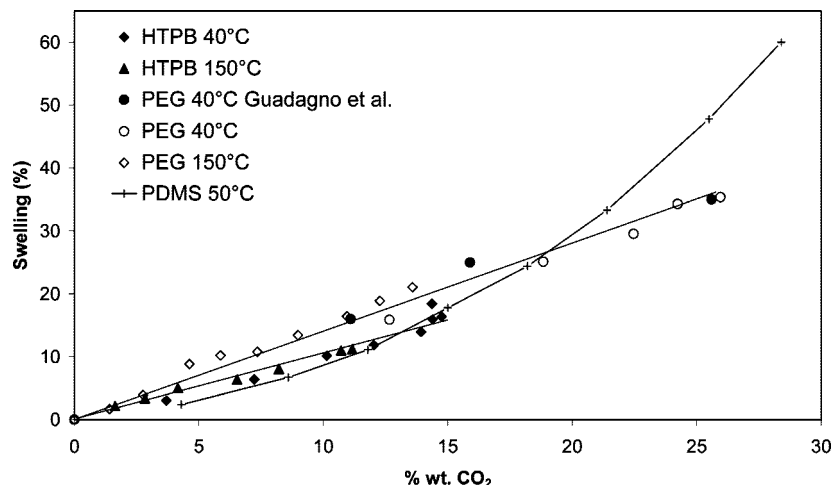


Figure 9. Swelling percentage of PEG, PDMS, and HTPB as a function of the weight percentage of CO₂ sorbed into the polymer.

Therefore, from these calculations, we have shown that the intermolecular interactions occurring between CO₂ and our model structures display the following energy order: $E(\text{PDMS}-\text{CO}_2) > E(\text{PEG}-\text{CO}_2) > E(\text{HTPB}-\text{CO}_2)$.

Since the solubility of CO₂ in these polymers follows the same order, we can consider that it is mainly driven by the CO₂–polymer interaction. Such conclusion is consistent with previous theoretical investigations,^{22,23,28} evidencing that other factors such as polymer–polymer interactions, CO₂–CO₂ interactions, as well as the solvent accessible surface area of CO₂ in connection with the free volume of the polymer have a much smaller influence on the ability of CO₂ to be sorbed into the polymer. Therefore, in order to obtain the higher gas sorption in a given polymer, the choice of an appropriate gas that will afford strong interactions with the main functional group of the polymer is required.

4.6. Analysis of the Correlation between CO₂ Sorption and Polymer Swelling. In order to determine how the swelling of the polymer and the CO₂ sorption are correlated, we have reported in Figure 9 the swelling percentage of PDMS, PEG, and HTPB as a function of the weight percentage of CO₂ sorbed into the polymer. For a given temperature in the pressure range investigated in this study, one can notice an almost linear dependence of the swelling of PEG and HTPB as a function of the weight percentage of CO₂ sorbed into the polymer. Such correlation has been found and discussed by other authors for semicrystalline polymers in supercritical CO₂.^{49,50} The temperature seems to have almost no effect on the slope of these curves. However, for a given weight percentage of CO₂ sorbed into the polymer, the swelling of PEG is higher than that observed for HTPB. In the case of PDMS, the swelling and CO₂ sorption are not linearly connected, and it appears that the swelling is higher than PEG and HTPB when the CO₂ sorption is above 25%.

Therefore, as expected above, the swelling of the polymer appears to be correlated to the CO₂ sorption since a higher CO₂ sorption will induce a higher swelling of the polymer. However, the correlation observed between the swelling and the CO₂ sorption is system specific and depends on several physical properties of the polymer such as the degree of crystallinity and crosslinking, the cohesivity (or the surface tension), the viscosity, and the chain flexibility.

5. Conclusion

Our experimental results extend the suitability of NIR spectroscopy, introduced in ref 18, to determine the CO₂ sorption

and polymer swelling as a function of temperature and CO₂ pressure. In particular, the swelling and CO₂ sorption reported here for the PEG–CO₂ system are in a very good agreement with literature data. In addition, new results have been obtained for this system at higher temperature, while the swelling and sorption for the HTPB–CO₂ system were reported for the first time. It has been found that the CO₂ sorption and swelling rate of PEG is higher than that measured for HTPB. In addition, the CO₂ sorption and swelling rate of both polymers are much lower upon an increase of temperature. Ab initio molecular orbital calculations on model structures and their complexes with CO₂ have been performed in order to identify at a molecular level the nature and strength of intermolecular interactions occurring between CO₂ and PDMS, PEG, and HTPB, which may be responsible for the observed differences in the solubility of CO₂ in these polymers. Results of energy calculations of the MTMS–CO₂, PME–CO₂, and 3-Hex–CO₂ dimers indicate that CO₂ interacts specifically with the three moieties through a Lewis acid–Lewis base type of interaction with the energies displaying the following order: $E(\text{MTMS}-\text{CO}_2) = -3.59 > E(\text{PME}-\text{CO}_2) = -3.43 > E(3\text{-Hex}-\text{CO}_2) = -2.5$ kcal/mol. Since the solubility of CO₂ in the corresponding homopolymers follows the same order, we can claim that the solubility of CO₂ in the polymer is mainly governed by the interactions between CO₂ and the main functional group of the polymer. This means that the stronger the interaction between CO₂ and the polymer, the higher the CO₂ sorption. Thus, it appears that even if one cannot exclude the influence of free volume and chain flexibility of the polymer, the role of such property seems to be less significant than the interaction between CO₂ and the polymer (as reported elsewhere^{22,23,28}).

Accordingly, the same trend is observed for the swelling of the polymer as a function of the CO₂ pressure. However, we have found that for a given CO₂ sorption in a polymer, its swelling depends on the nature of the polymer. The swelling is certainly not only controlled by the CO₂–polymer interactions but also by other specific properties of the polymer such as its cohesivity (or the surface tension), its viscosity, and the chain flexibility.

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