

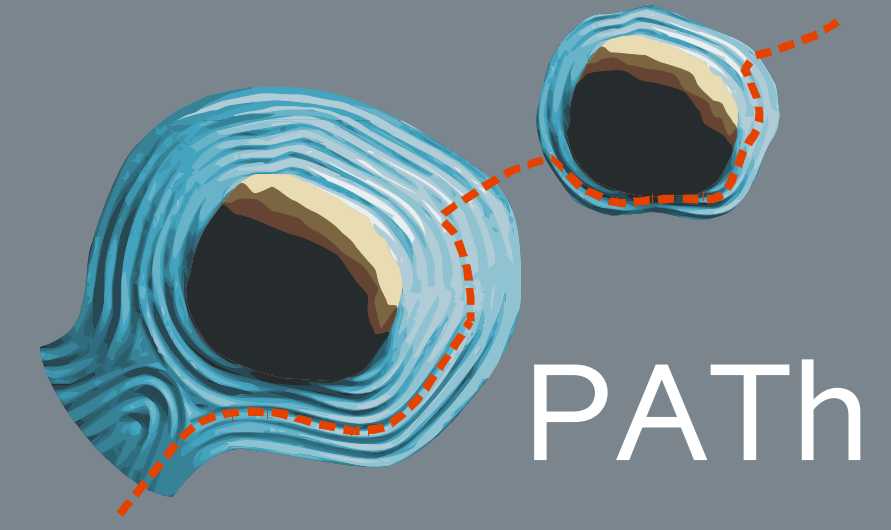
# GAS SORPTION IN POLY(LACTIC ACID)

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## 1. Introduction

**Poly(lactide) polymers** (PLA) have received increasing attention in the last decade due to their natural biodegradability. They have been used since 1970s for biomedical and pharmaceutical applications, but only recently the technology for large scale fabrication has been fully developed, making PLA available at low cost for innumerable other applications. In addition to being thermoplastic, biodegradable, compostable and produced from annually renewable feedstock, PLA show mechanical and barrier properties similar to synthetic polymers that have been long used for food packaging, like poly(styrene) (PS) and polyethylene terephthalate (PET).

The objective of this work is to study the mechanism of gas/vapor solubility in Poly(Lactic Acid) (PLA) and to provide some insight on the effect of the temperature conditioning on the gas sorption in the polymer film. For that purpose, the solubility of carbon dioxide, oxygen, nitrogen, ethylene and water vapor in Poly(Lactic Acid) (PLA) in temperature range from 283 to 323 K and up to 1 bar, was measured using a **Quartz Crystal Microbalance** (QCM). In order to address the pressure effect, CO<sub>2</sub> equilibrium sorption values were also measured up to 50 bar.

Three distinct thermal treatments, annealed, melted and quenched, were performed and the experimental data obtained was analyzed with the dual mode sorption model. In order to address the effect of crystallinity and stereochemistry, 2 different (L:D) contents were used, 80:20 and 98:2.

## 2. Experimental

The QCM was the experimental technique used to measure the sorption of the atmospheric gases and vapors in PLA as well as ethylene. In this method the gas sorption is related to the frequency change of the quartz crystals coated with the polymer under study before and after the gas/vapor sorption. This method is very useful since it requires short equilibration times, while retaining the good accuracy of traditional methods. A detailed description of both apparatuses can be found at [1, 2].

The gas solubility is calculated by:

$$C(v/v) = \frac{(\Delta F_E - \Delta F_{P,V}) \rho_{pol} \cdot 22416}{\Delta F_C M_{gas}}$$

where  $\Delta F_E$  is the measured frequency change of the working crystal,  $\Delta F_{P,V}$  is the frequency change of the reference crystal and  $\Delta F_C$  is the frequency change of the polymer mass on working crystal,  $\rho_{pol}$  is the polymer density, 22416 is the gas molar volume at STP and  $M_{gas}$  is the gas molecular weight.

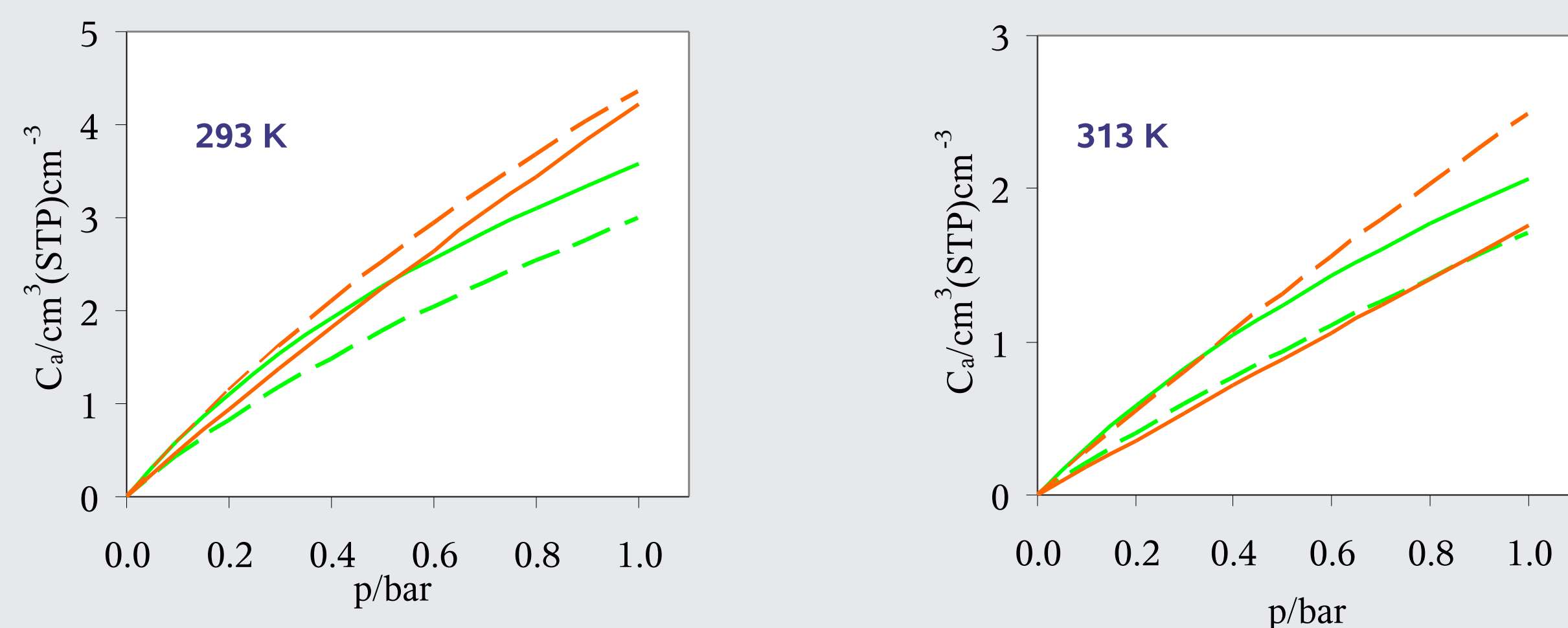
It has been showed that glassy polymers have an extended thermal memory and it is thus very interesting to study the effect of thermal treatment in the thermodynamic properties. The PLA coated quartz crystal submitted to **three different thermal protocols**:

- annealing**, which consists on heating the polymer film at 336 K for 1 day, cool it down to ambient temperature for 1 day and heating it up again at 336 K for 1 day more
- melting**, which consists on heating it up to 523 K at 2 K/min and cool it down to ambient temperature at 10 K/min;
- quenching**, heating it up to 523 K at 2K/min and cool it down to 259 K.

All the thermal protocols influence the **crystallization** percentage for PLA 98:2, changing it 46% if no temperature treatment is performed to 20%, 10 % and 5 %, to the annealing, melting and quenching treatments, respectively. PLA 80:20 is strictly amorphous.

## 3. Results

The solubility of CO<sub>2</sub> at 293 and 313 K up to 1 bar are presented in Figure 1 for PLA 80:20 and 98:2 with the melting and the annealing protocols. It was observed that the CO<sub>2</sub> sorption results for the quenched thermal treatment are very similar to one of the other and thus are not represented here. The results for the other 3 temperatures show similar behavior.



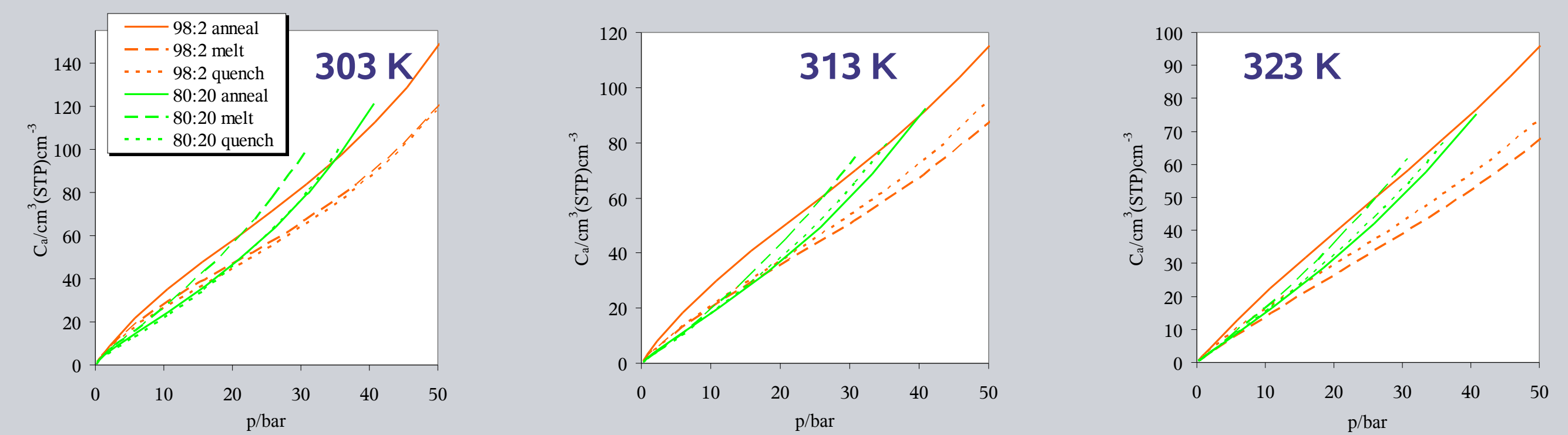
**Figure 1:** Carbon dioxide solubility at low pressure in PLA 80:20 and 98:2 with two thermal treatments. (—) PLA 80:20 annealed, (---) PLA 80:20 melted, (—) PLA 98:2 annealed and (---) PLA 98:2 melted.

The solubility results for PLA 98:2 annealed, melted and quenched were corrected by a factor of 1.25, 1.11 and 1.05, respectively, considering that the crystalline regions do not accommodate any gas. The solubility decreases with temperature for the same polymer with the same temperature protocol. It can be observed that for the same temperature the solubility of CO<sub>2</sub> is usually larger in PLA 80:20 than in PLA 98:2 for the same thermal treatment, indicating an **influence of stereochemistry of the polymer on the gas sorption**. For **PLA 98:2**, the **annealing treatment leads to a larger solubility of CO<sub>2</sub>** than the melted one. This is in agreement with concept of excess free volume, which should be smaller in the annealing treatment since it has a larger relaxation time. For **PLA 80:20 the reverse behaviour** was found.

In Figure 2, the solubility of CO<sub>2</sub> at high pressure in PLA 80:20 and 98:2 with three thermal treatments, is presented.

## References

- [1] Oliveira, N S, Oliveira, J, Gomes, T, Ferreira, A, Dorgan, J, Marrucho, I M, *Fluid Phase Equilib.* **222-223** (2004) 317.  
 [2] Oliveira, N S, Dorgan, J, Coutinho, J A P, Ferreira, A, Daridon, J L, Marrucho, I M, *Journal of Polymer Science: Part B: Polymer Physics*, **44** (2006) 1010-1019.

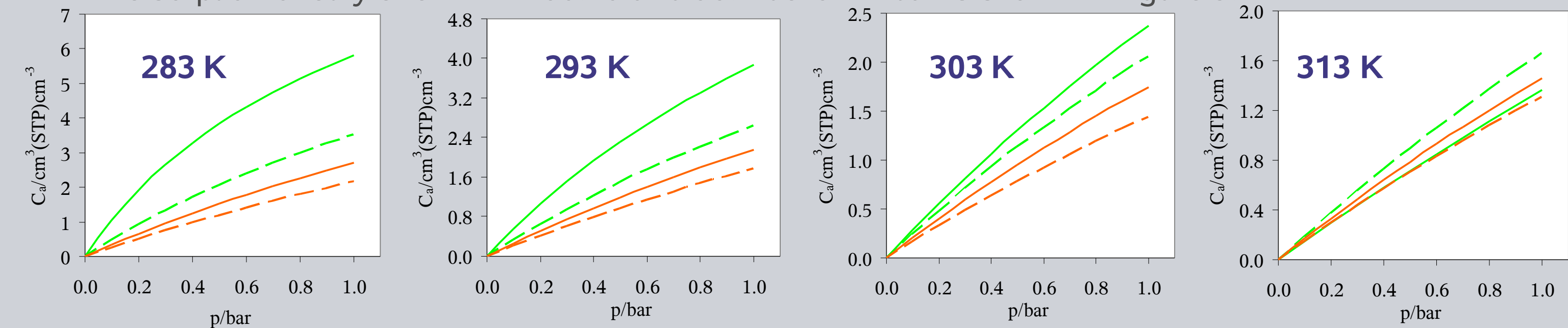


**Figure 2:** Carbon dioxide solubility at high pressure in PLA 80:20 and 98:2 with three thermal treatments.

The results obtained for high pressures indicate that CO<sub>2</sub> is slightly more soluble in PLA 80:20 than in PLA 98:2, especially at higher pressures. This is probably due to a **swelling effect in PLA 80:20**, since the isotherms present a convex curvature with respect to the pressure axis, while the PLA 98:2 isotherms exhibits a more linear behavior, indicating the absence of swelling. This fact can be associate to the **presence of crystallites in PLA 98:2 that can restrict the chain mobility** in the amorphous phase, acting as virtual cross-linkers, thus reducing the volume available for the penetrant to make a diffusional jump and also avoiding the swelling.

The experimental solubility results at low pressure were correlated by the **Dual-Mode Sorption Model** and at high pressure the **Flory-Huggins/Langmuir Sorption Model** was used. These models are depicted as lines in the Figures.

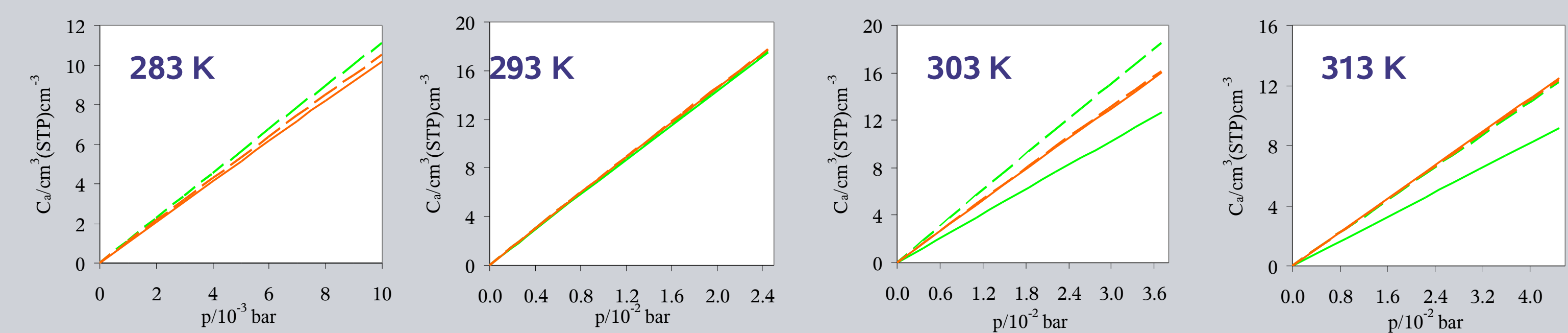
The sorption of ethylene in PLA 80:20 and 98:2 below 1 bar is shown in Figure 3.



**Figure 3:** Ethylene solubility at low pressure in PLA 80:20 and 98:2 with two thermal treatments. (—) PLA 80:20 annealed, (---) PLA 80:20 melted, (—) PLA 98:2 annealed and (---) PLA 98:2 melted.

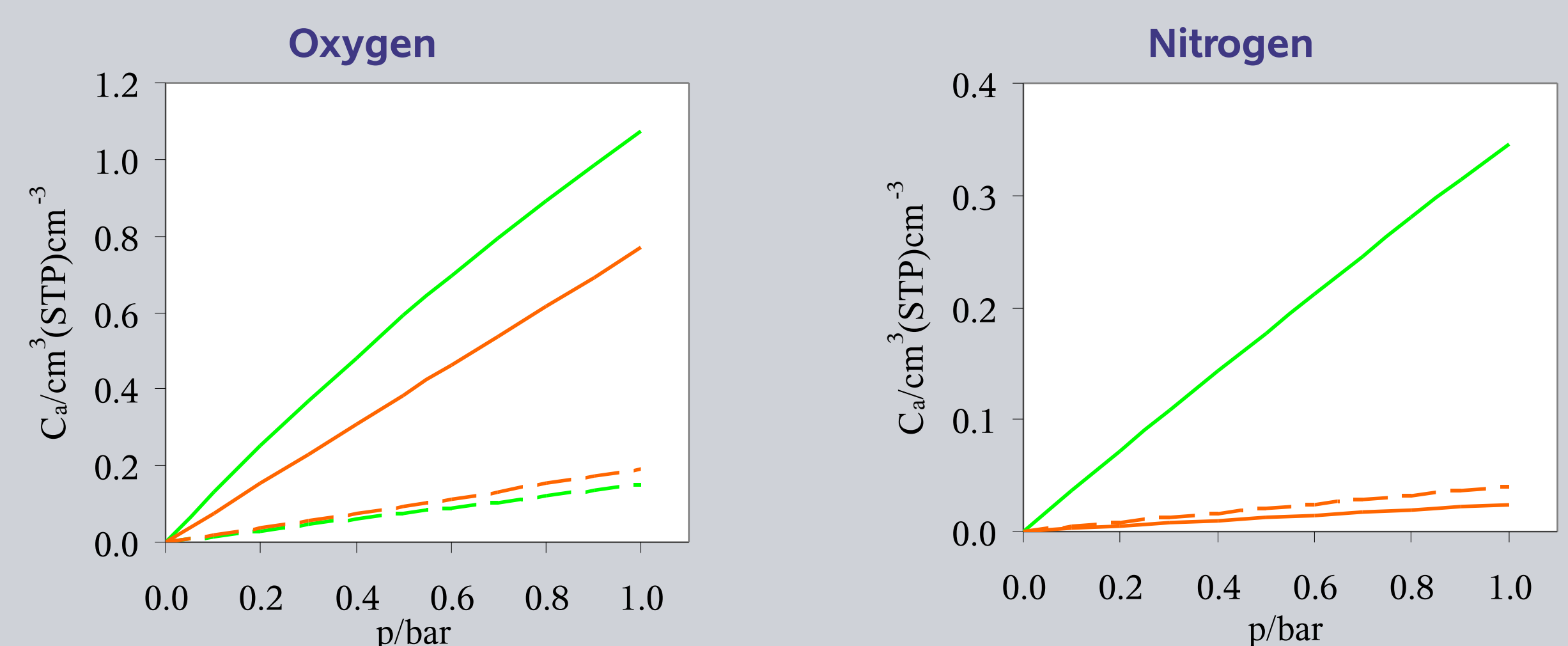
This gas presents a higher sorption in PLA 80:20 than in PLA 98:2, indicating that sorption is related to isomer percentage. However, the thermal treatment also has influence in the gas sorption, since the sorption is higher for annealed films when compared with melted films.

The Figure 4 presents the solubility of water vapor in PLA 80:20 and 98:2. The stereochemistry and thermal treatment have little effect in the solubility, comparable with the effect in other gases.



**Figure 4:** Water vapor solubility at low pressure in PLA 80:20 and 98:2 with two thermal treatments. (—) PLA 80:20 annealed, (---) PLA 80:20 melted, (—) PLA 98:2 annealed and (---) PLA 98:2 melted.

O<sub>2</sub> and N<sub>2</sub> solubility in PLA 80:20 and 98:2 is presented in Figure 5 at 303 K. It can be observed that these two gases are very little soluble in both PLAs, especially nitrogen. It can be observed that for both O<sub>2</sub> and N<sub>2</sub>, the (L:D) ratio does not play a significant role in sorption, while the temperature protocol affects it.



**Figure 5:** Oxygen and nitrogen solubility at low pressure in PLA 80:20 and 98:2 with two thermal treatments. (—) PLA 80:20 annealed, (---) PLA 80:20 melted, (—) PLA 98:2 annealed and (---) PLA 98:2 melted.

## 4. Conclusions

- ✓ The magnitude of the solubility of gases in PLA follows the same order as the condensability of each gas/vapour.
- ✓ Both PLA 98:2 and 80:20 have thermal memory that affects the gas/vapour sorption. The gas sorption is larger in annealed films, probably due to a smaller excess free volume, since this protocol has longer relaxation times
- ✓ At high pressure, PLA 80:20 swells while PLA 98:2 does not swell, probably due to the presence of crystallites.
- ✓ At low pressure, there is no distinction between the melted and the annealed protocols, in terms of gas solubility.

## Acknowledgments

Nelson S. Oliveira thanks Fundação para a Ciência e a Tecnologia for the Ph.D. scholarship (SFRH/BD/6690/2001).