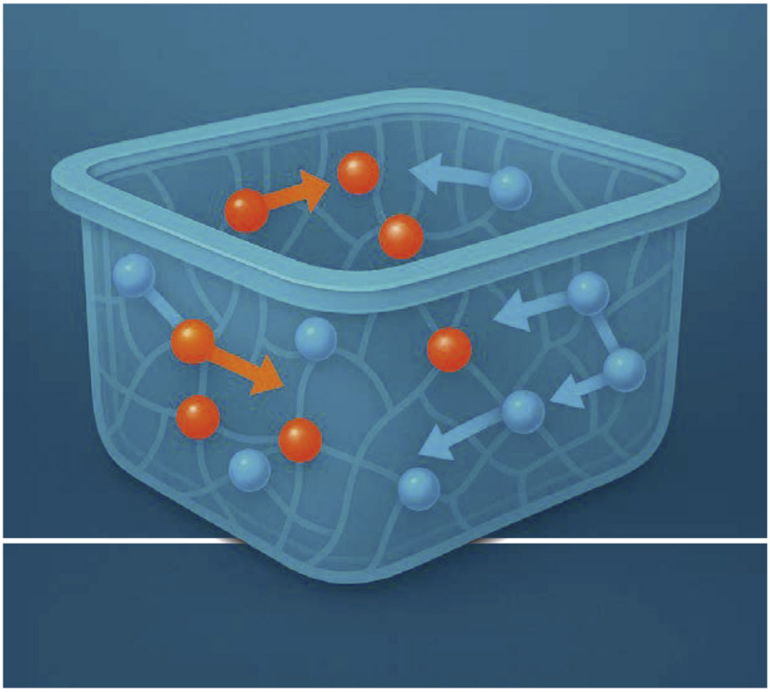
Agustín Ríos de Anda
Paul Sotta

Sorption and Diffusion in Polymers

Functional Materials and Applications



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Dr. Agustín Ríos de Anda is a Professor at Ingénierie des Matériaux Polymères (Polymer Materials Engineering), a joint CNRS/Université Lyon/INSA Lyon lab in Lyon, France since September 2025. After obtaining his engineering degree in polymer chemistry in 2009 from the Institut National des Sciences Appliquées de Rouen, France, he undertook his PhD under Dr. Paul Sotta and Dr. Louise-Anne Fillot at the Advanced Polymers and Materials Laboratory in Lyon, France. His dissertation, presented in 2012, dealt with the influence of sorption of polar and non-polar molecules in nylon 6,6 and the consequences of such sorption and diffusion on the polymer's mechanical properties. He then conducted two postdoctoral periods of research at the University of Bayreuth, Germany, under Prof. Volker Altstädt, and at the Centre de Recherche sur les Macromolécules Végétales, Grenoble, France, under Dr. Laurent Heux. From September 2016 to August 2025 he held a tenure as Associate Professor at Université Paris Est Créteil. He has specialized in investigating the relationship between polymers' chemical and morphological structure with their macroscopic mechanical and transport properties through a multiscale experimental approach. For the past several years he has focused his research and this approach on bio-based functional polymers.

Dr. Paul Sotta

Dr. Paul Sotta is Senior CNRS Researcher at Ingénierie des Matériaux Polymères (Polymer Materials Engineering), a joint CNRS/Université Lyon/INSA Lyon lab in Lyon. He obtained his PhD in 1987 at the Université Paris-Sud (now Université Paris-Saclay), and then was a CNRS researcher at Laboratoire de Physique des Solides, a joint CNRS/Université Paris-Sud lab (1988–2006), invited researcher in the group of H. W. Spiess at the Max-Planck-Institut für Polymerforschung, Mainz, Germany (1995–1996), and CNRS senior researcher at the Laboratoire Polymères et Matériaux Avancés, a joint CNRS/Solvay lab in Lyon (2006–2020). He has made major scientific contributions in polymer physics, namely in local structure and dynamics in elastomers and reinforced elastomers, glass transition, reinforcement mechanisms, tear and wear resistance, polymer blends, deformation mechanisms in semicrystalline polymers, and solvent sorption in polymers. His fields of expertise cover both modeling and experimental techniques such as broadband dielectric spectroscopy, pseudo-solid NMR, X-ray and neutron scattering, tribology and contact mechanics, linear and non-linear rheology and mechanics.

The Contributors

Chapter No.	Title	Contributors
1	Modelling Solvent Sorption in Polar Polymers using a Physical, Isothermal, Non-Empirical Model	Agustín Rios de Anda, Paul Sotta
2	Influence of Organic Solvent Sorption upon Water Infiltration and Molecular Mobility in Polyamides	Agustín Ríos de Anda, Florentina-Maria Preda, Louise-Anne Fillot, Paul Sotta
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4	Permeability of Oxygen through Polymers	Emmanuel Richaud, Alain Guinault
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Preface

One of the largest and most important applications of polymers has been, for several decades, their use as barrier materials. These applications range from the cellophane or polystyrene films used in food packaging to the use of technical polymers in oil and gas exploration and transportation. Among these numerous applications, the most common are the use of PET for liquid bottles and PE for milk bottles, PVC hoses for gardening and water circuits in buildings, polyamides in hoses at gas stations, polyfluorovinyls for raincoats and umbrellas, and polyvinyl alcohol for contact lenses, to mention a few. Novel barrier applications of polymers are found in the automotive industry where polyamides have been considered to be used in the fuel circuit (i. e. as gas tanks and also as the hoses connecting the tank with the engine). Other important current barrier/transport applications of polymers are as smart membranes for the controlled release of pharmaceuticals and as chemical sensors in medical applications. Further applications are found in the vast field of bladders of all kinds like in the tire industry, and sports applications (balls, equipment, etc.). Another key application is the large field of O-rings and sealings of all kinds, which are ubiquitous in vehicles as well as in gas, oil, and liquid transportation.

However, these barrier/transport properties are often neglected or relegated to the background behind their thermal, mechanical, and optical behavior. They are very often considered only from an engineering point of view. This means that tests performed to characterize the materials are engineering, normalized tests which deliver performance indices rather than well-defined physical quantities. This also means that most often empirical models are used to tentatively predict the performances of new materials by inter- or extrapolating the performance of known materials.

This book covers a theoretical part of transport phenomena, but focuses mostly on areas important to both academia and industry.

Several authors have studied these properties since the boom of such materials in the 1940s, the most well-known being Langmuir, Flory & Huggins, and Crank. Since then, several models of sorption of gas and/or liquid molecules in polymers have been proposed over the years to better understand and describe the various sorption mechanisms observed in polymers, especially in the case where molecules have strong affinities with the polymers and/or form so-called clusters within the materials. These models, which are presented in this book, describe well the sorption of solvents through a combination of a physical approach with empirical observations. These approaches yield qualitative parameters that are not able to completely describe the observed sorption phenomena physically. Thus, as an introductory part of this book a purely physical new model is proposed to describe the sorption of molecules having strong affinities with polymers possessing preferential sorption/interaction sites. This model yields physically meaningful parameters that describe the sorption of a given polymer/solvent system.

Subsequently in the book, transport phenomena in various applicative and functional polymers are discussed, with a focus on how to enhance such properties. Several areas relevant to the research and engineering fields on barrier/transport properties are thus considered, such as areas in which barrier properties are of direct, primary relevance in the application: fuel tanks and hoses, water and/or fluid circuitry, bladders, food packaging, and O-rings and sealings. While the barrier property is the primary concern, the final application often demands a compromise between barrier properties and other properties such as mechanical toughness (e. g. for fuel tanks), electrical insulation, etc., be achieved. Sometimes, optimizing both barrier properties and, for example, mechanical properties demands adjustment of some material feature in an antagonistic way. One example is the role of the glass transition temperature of the polymer. Decreasing solvent diffusion can be achieved by increasing the glass transition of the polymer, which means decreasing the molecular mobility at usage temperature, but this may make the polymer fragile, which is critical as regards its toughness.

This book aims thus to summarize and condense the latest research in the field of sorption, diffusion, and permeation in functional polymers.

A. Ríos de Anda, P. Sotta

July 2025

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1 Modelling Solvent Sorption in Polar Polymers using a Physical, Isothermal, Non-Empirical Model

Agustín Ríos de Anda and Paul Sotta

1.1 Introduction

One of the largest and most important applications of polymers has been, for several decades, their use as barrier materials. These applications range from the cellophane or polystyrene films covering our food in supermarkets to the use of technical polymers in oil and gas exploration and transportation. Amongst these applications, the most common ones are the use of PET for liquid bottles and PE for milk bottles, PVC hoses for gardening and water circuits in buildings, polyamides in hoses at gas stations, polyfluorovinyls for raincoats and umbrellas, and polyvinyl alcohol for contact lenses, to mention a few. Novel barrier applications of polymers are found in the automotive industry, where polyamides have been considered for use in the fuel circuit (i. e. as gas tanks and also as the hoses connecting the tank with the engine) and technical metal-plated carbon-fiber-reinforced epoxides for hydrogen storage. Other important current barrier/transport applications of polymers are as smart membranes for the controlled release of pharmaceuticals, and as chemical sensors in medical applications.

However, these barrier/transport properties are often neglected or relegated to second place in front of their thermal, mechanical, and optical behavior. Nevertheless, several authors have studied these properties since the boom of these materials in the 1940s, the most well-known being Langmuir [1], Flory & Huggins [2–9], and Crank [10].

Since then, several models of sorption of gas and/or liquid molecules in polyamides have been proposed to better understand and describe the various sorption mechanisms observed in polymers, especially in the case where molecules have strong affinities with the polymers and/or form so-called clusters within the materials. These models, which will be presented and detailed in Section 1.2, describe well the sorption of solvents through a combination of a physical approach with empirical observations. However, these approaches yield qualitative parameters that are not able to completely physically describe the observed sorption phenomena.

To resolve this deficit, in Section 1.3 we describe a new, purely physical model describing the sorption of molecules with strong affinities to polymers that possess preferential sorption/interaction sites. We show that this model yields physically meaningful parameters that describe the sorption of a given polymer–solvent system. A comparison of the predictions of this model with experimental data is then provided in Section 1.4.

1.2 Sorption Mechanisms in Polymers

1.2.1 Sorption Thermodynamics

When a polymer is put into contact with a solvent under partial vapor pressure P, the solvent molecules penetrate into the polymer matrix up to a certain equilibrium concentration given by:

$$\mu_s(c, T) = \mu_{gas}(P, T) \tag{1.1}$$

Where:

$\mu_s(c, T)$ = chemical potential of sorbed molecules, which depends on the concentration c in the material and on T

$\mu_{gas}(P, T)$ = chemical potential of the gas, given by:

$$\mu_g(P, T) = RT \ln\left(\frac{P}{P_{sat}}\right) = RT \ln a \tag{1.2}$$

Where:

a = chemical activity

The chemical potential of the saturating vapor (gas at $P = P_{sat}$) is $\mu_g^{(0)}(T)$, and this vapor is in equilibrium with the liquid (thus $\mu_g^{(0)}(T) = \mu_{liq}(T)$), and has been chosen as the zero level of chemical potential. Then $\mu_{gas}(P, T)$ is negative if $P < P_{sat}$. For the gas phase at fixed pressure P, P/P_{sat} decreases as T increases. Thus, the chemical potential μ_{gas} decreases as T increases, and sorption decreases as T increases. The chemical potential of the liquid (which is nearly independent of P), which corresponds to a fixed activity $a = 1$, increases as T increases. Thus, in this case, the sorption increases as T increases. More generally, at a given, fixed activity $a = P/P_{sat}$ (which corresponds to a partial pressure of the gas P increasing as T increases), the chemical potential increases as T increases. Thus, the sorption increases as T increases.

The sorption thermodynamics is illustrated in Figure 1.1. Sorption isotherms, which relate the concentration c in the material to the pressure P or activity a of the vapor at a temperature T, are described by Equation 1.1. The chemical potential may be written $\mu_{ads}(c, T) = \Delta H - T\Delta S$, with an enthalpic contribution (enthalpy of sorption ΔH) and an entropic term ΔS, which depends on concentration c. Note that ΔH may possibly depend on temperature.

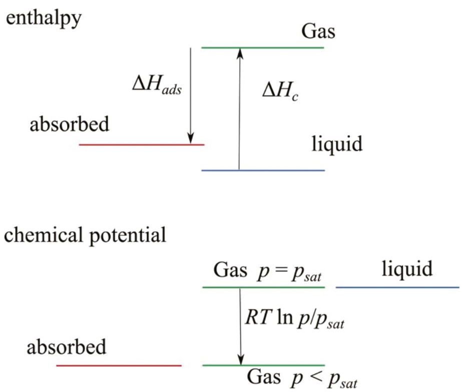

Figure 1.1 Thermodynamic relations related to sorption

By measuring sorption isotherms at various temperatures T and taking points at constant concentration c, the following curve is obtained [11]:

$$\ln a_c(T) = \frac{\Delta H_{st}}{RT} + \text{constant} \tag{1.3}$$

Then ΔH_{st} (at a given concentration c) can be obtained from the slope of the curve ln ac vs $1/T$. This quantity is called the net isosteric heat of sorption, and is equal to $\Delta H_{st} = \Delta H_{abs} - \Delta H_{cond}$.

The sorption enthalpy $\Delta H_{abs} = H_{gas} - H_{abs}$ contains the contribution of molecular interactions of water molecules in an adsorbed state compared to water molecules in a gaseous state. In order to compare the interactions of water molecules sorbed in the polymer to those in liquid water, the heat of liquefaction ΔH_{cond} must be subtracted [11] (Figure 1.1). Note that Equation 1.3 is analogous to the Clapeyron equation for liquefaction [12] $\frac{\partial \ln P_{sat}}{\partial \mathrm{T}} = \frac{\Delta H_{vap}}{T^2}$, where ΔH_{vap} is the enthalpy of vaporization.

1.2.2 Sorption Models

Several models have been developed in order to relate the equilibrium penetrant concentration to the penetrant activity, i. e., to describe the shape of sorption isotherms. The simplest one is Henry's law [13–15]. This model applies to the sorption of ideal gases at low activities, and states that at a constant temperature, the amount of gas