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TESIS DOCTORAL:

HIGH POROSITY POLYMERS FOR ADVANCED APPLICATIONS

Presentada por Isabel Noelia Esteban Hernández
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CERTIFICAN:

Que la memoria titulada ***"High Porosity Polymers For Advanced Applications"*** presentada por **Dña. I. Noelia Esteban Hernández** para optar al grado de Doctora ha sido realizada bajo nuestra supervisión en el grupo CLiNuMat del I.U. CINQUIMA en el Departamento de Química Inorgánica de la Universidad de Valladolid y en el grupo de Grupo de Policondensación y Membranas Poliméricas del ICTP-CSIC.

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La presente Tesis Doctoral titulada ***“High Porosity Polymers For Advanced Applications”*** aspira a obtener la mención de Doctorado Internacional (Artículo 22, BOCyL núm. 96 del 20 de mayo, págs. 23821-23846 y corrección de errores publicada en BOCyL núm. 98 del 24 de mayo, pág. 24331). La memoria ha sido redactada en inglés incluyendo los apartados Abstract y Conclusions redactados también en español.

Esta Tesis Doctoral ha sido realizada en el grupo de investigación Cristales Líquidos y Nuevos Materiales (CLiNuMat) del IU CINQUIMA y en el Grupo de Policondensación y Membranas Poliméricas del ICTP-CSIC bajo la dirección y supervisión de Jesús A. Miguel, Ángel E. Lozano y Cristina Álvarez.

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“Nothing in life is to be feared, it is only to be understood.

Now is the time to understand more, so that we may fear less”

Marie Curie

Summary

Abstract

Research on improved catalysts is in high demand by industry because they are chemicals of great interest for their use in a wide variety of industrial processes. Catalysts enhance operating conditions, increase reaction rates, reduce costs, time, and environmental problems associated with their use by decreasing toxic by-products of manufacturing. Porous polymers with chelating groups in their structures, while exhibiting good chemical and thermal stabilities and high surface areas, are attractive catalytic precursors, allowing them to become heterogeneous catalysts, which can be effectively used in high-demanded catalytic reactions.

For this purpose, in this Ph. D. research memory polymers based on different chelating precursors (one of them having a bipyridine moiety formed by modification of 4,5-diazafluoren-9-one (DF) and the other ones, having anchored aromatic diphosphines; 1,2-bis(diphenylphosphino)ethane (DPPE), 1,3-bis(diphenylphosphino)propane (DPPP), 1,4-bis(diphenylphosphino)butane (DPPB)) inside of the material have been obtained.

DF is an activated ketone due to the presence of nitrogen atoms in their bipyridine structure. In this context, DF can be used as an electrophilic monomer in hydroxy-alkylation polymerization (S_EAr) reactions, which are activated by using a superacid as a promotor. In the first stage of the research, the reactivity of DF was studied and compared with isatin (IS) and N-methyl-isatin (MeIS) employing S_EAr conditions. It was shown that, despite having lower reactivity than IS and MeIS, DF can form high molecular weight polymers when the reaction is optimized. Then, two families of polymers derived from DF could be efficiently obtained and studied in gas separation and catalytic applications. The first family of polymers consisted of the synthesis of a homopolymer using biphenyl (BP) as a nucleophilic aromatic difunctional monomer and in the synthesis of copolymers employing IS and MeIS as electrophilic comonomers. These polycondensation reactions gave rise to linear polymers (LP) with sufficient molecular weight to be processed as films with good mechanical properties. The second family consisted of the synthesis of polymeric networks obtained using 1,3,5-triphenylbenzene (135TPB) as a nucleophilic trifunctional aromatic monomer and DF (and in some materials mixtures with IS) as electrophilic monomer, giving rise to amorphous three-dimensional porous polymeric networks (POPs). Both families, due to the high number of aromatic moieties, together with the presence of non-labile bonds, in their structures showed excellent thermal and chemical stabilities, with degradation temperatures well above 400 °C.

In particular, the first family of polymers was synthesized using a stoichiometric molar ratio between the nucleophile and the electrophile. As commented above, BP was the nucleophile and DF, IS, MeIS, or mixtures of DF/IS or DF/MeIs in equimolar ratios were used as electrophiles. Trifluoromethane sulfonic acid (TFSA) was used as the promotor acid and chloroform as the cosolvent. Due to the difference in reactivity of DF with IS and MeIS, the polymerization reaction had to be optimized to obtain polymers with enough molecular weight. The thermal stability of the polymers derived from DF was superior to that of non-DF-derived polymers. The DF-derived polymers exhibit a high glass transition temperature above 375 °C. The permeability values were slightly lower than those observed for the analogous IS and MeIS-derived polymers. However, it was observed that the bipyridine groups could be monoprotonated and that the protonated films possessed excellent separation capabilities, particularly when the gas was CO_2.

The second family consisted of POPs having a bipyridine moiety, which were used as catalytic supports. First off, the POPs were synthesized using a stoichiometric ratio between the 135TPB nucleophile, and difunctional electrophiles; DF, alone or copolymerized with IS. To optimize the polymerization reaction, these POPs were synthesized using different reaction conditions (temperature, time, and use, or not, of chloroform as cosolvent). After characterizing the POPs some of them were selected for their use as catalytic precursors. These amorphous POPs showed thermal stabilities higher than 500 °C with char yield at 800 °C above 70%, and high surface areas from 760 to 935 m^2/g showing a large microporosity contribution. Finally, the POPs, which contain bipyridine moieties, were able to anchor palladium(II) acetate, giving rise to heterogeneous palladium catalysts, which were used in Suzuki-Miyaura reactions using a green solvent. The catalytic materials, even at low palladium loads showed excellent catalytic conversions. Moreover, these heterogeneous catalysts could be recycled with any significant loss of activity and leaching for at least five runs.

In other research of this memory, due to the metal coordinating capacity of the phosphorous atom of aromatic diphosphines and the versatility of the known as *knitting* synthetic methodology for making polymer network materials from aromatic compounds, new hypercrosslinked microporous polymers were synthesized by reacting a diphosphine (DPPE, DPPP or DPPB) with 135TPB, or a mixture of 135TPB and BP (used as aromatic comonomer), using dimethoxymethane as a crosslinking agent, iron(III) chloride as Lewis acid and 1,2-dichloroethane as solvent. These POPs showed moderate thermal stabilities, high chemical stability, and high surface areas between 760 and 1300 m^2/g. The polymer networks, synthesized using BP as a comonomer, exhibited high microporosity while the materials obtained not using BP showed a higher mesoporous contribution. Consequently to their synthesis, confined heterogeneous catalysts were prepared from these network materials by coordinating palladium(II) acetate, and were tested in Suzuki-Miyaura cross-coupling reactions using green solvents and aerobic conditions, displaying excellent conversions. Furthermore, these catalysts could be recycled for at least five runs without loss of catalytic activity or leaching.

Resumen

La búsqueda de nuevos catalizadores que aúnen las ventajas de los catalizadores homogéneos y heterogéneos es altamente demandada por la industria ya que su uso es necesario en la mayoría de los procesos químicos. Los catalizadores no solo mejoran las condiciones de funcionamiento aumentando la velocidad de reacción o permitiendo el uso de condiciones más suaves, sino que también su uso conduce a una reducción de los costes, del consumo energético y de la formación de subproductos tóxicos, disminuyendo los problemas medioambientales asociados a su uso. Por ellos, en esta memoria de tesis por compendio se han desarrollado materiales poliméricos a partir de monómeros capaces de complejar metales en su estructura, y así poder ser empleados en distintas aplicaciones, concretamente en catálisis heterogénea.

Para la preparación de las distintas familias de polímeros desarrolladas en este trabajo se seleccionaron como monómeros bidentados la bipiridina 4,5-diazafluoren-9-ona (DF) y las difosfinas aromáticas 1,2-bis(difenilfosfino)etano (DPPE), 1,3-bis(difenilfosfino)propano (DPPP) y 1,4-bis(difenilfosfino)butano (DPPB).

DF es una cetona activada debido a la presencia de átomos de nitrógeno en su estructura de bipiridina. En este contexto, el monómero DF puede utilizarse como electrófilo en reacciones de polimerización por hidroxialquilación (sustitución electrófila aromática, S_EAr), que se activan utilizando un superácido como promotor. En la primera etapa de la investigación, se estudió la reactividad de DF y se comparó con la reactividad de isatina (IS) y N-metil-isatina (MeIS) empleando condiciones S_EAr. Se demostró que, a pesar de tener menor reactividad que los monómeros IS y MeIS, el monómero DF puede formar polímeros de alto peso molecular cuando se optimiza la reacción. Por ello, en la siguiente etapa, tras optimizar las reacciones, se obtuvieron dos familias de polímeros derivados de DF que se usaron en aplicaciones catalíticas y de separación de gases.

La primera familia de polímeros consistió en la síntesis de polímeros lineales (LPs) empleando bifenilo (BP) como monómero difuncional aromático nucleófilo. Para ello se sintetizaron un homopolímero usando DF como único monómero electrófilo y copolímeros empleando IS y MeIS como comonómeros electrófilos. Debido a la diferencia de reactividad de DF con IS y MeIS, fue necesario optimizar la reacción de polimerización para obtener polímeros con suficiente peso molecular. Tras optimizar las reacciones, esta familia se sintetizó usando una relación molar estequiométrica entre electrófilo y nucleófilo. Para la síntesis de los copolímeros, las mezclas de monómeros electófilos empleada fue en proporciones equimolares DF/IS y DF/MeIS. Como ácido promotor se utilizó ácido trifluorometano sulfónico (TFSA) y cloroformo como

cosolvente. Los polímeros derivados de DF presentaron una estabilidad térmica superior a la de los polímeros sintetizados sin usar dicho monómero y una elevada temperatura de transición vítrea por encima de 375 °C. Estas reacciones de policondensación dieron lugar LPs con peso molecular suficiente para ser procesados como *filmes* con buenas propiedades mecánicas. Al evaluarse en separación de gases, se observó que los valores de permeabilidad de los LPs derivados de DF fueron ligeramente inferiores a los observados para los polímeros análogos derivados de IS y MeIS. Sin embargo, se observó que los grupos bipiridina podían monoprotonarse y que las películas protonadas poseían una excelente capacidad de separación, especialmente cuando el gas era CO_2.

La segunda familia consistió en la síntesis de redes poliméricas obtenidas utilizando 1,3,5-trifenilbenceno (135TPB) como monómero aromático trifuncional nucleófilo y DF (o mezclas de DF con IS) como monómero electrófilo, dando lugar a redes poliméricas porosas tridimensionales amorfas (POPs). En primer lugar, los POPs se sintetizaron utilizando una proporción estequiométrica entre el nucleófilo 135TPB, y electrófilos difuncionales (DF solo o copolimerizado con IS). Para optimizar la reacción de polimerización, estos POP se sintetizaron utilizando diferentes condiciones de reacción (temperatura, tiempo y uso, o no, de cloroformo como cosolvente). Tras caracterizar los POPs se seleccionaron algunos de ellos para su uso como precursores catalíticos. Estos POP amorfos mostraron estabilidades térmicas superiores a 500 °C, con un residuo carbonado superior al 70% a 800 °C, y elevadas áreas superficiales entre 760 y 935 m^2/g que mostraban una gran contribución de la microporosidad. Una vez caracterizados, estos POPs se utilizaron como soportes catalíticos anclando en ellos acetato de paladio(II). Estos catalizadores heterogéneos de paladio se estudiaron en reacciones de Suzuki-Miyaura utilizando un disolvente verde. Dichos materiales catalíticos, incluso a bajas cargas de paladio, mostraron excelentes conversiones catalíticas y pudieron reciclarse sin pérdida significativa de actividad ni *leaching* durante al menos cinco ciclos.

Ambas familias derivadas del monómero DF, debido al elevado número de moléculas aromáticas, junto con la presencia de enlaces no lábiles, mostraron en sus estructuras una excelente estabilidad térmica y química, con temperaturas de degradación muy superiores a 400 °C.

Por otro lado, teniendo en cuenta la capacidad de coordinación metálica del átomo de fósforo de las difosfinas aromáticas y a la versatilidad de la metodología sintética conocida como *knitting* para fabricar materiales poliméricos hiperreticulados, tres nuevas familias de polímeros porosos fueron sintetizadas haciendo reaccionar una difosfina aromática (DPPE, DPPP o DPPB) con 135TPB, o una mezcla de 135TPB y BP (utilizada como comonómero aromático), utilizando dimetoximetano como agente reticulante, cloruro de hierro como ácido de Lewis y 1,2-dicloroetano como disolvente. Estos POP mostraron estabilidades térmicas moderadas, alta estabilidad química y elevadas áreas superficiales entre 760 y 1300 m^2/g. Las redes poliméricas, sintetizadas utilizando BP como comonómero, mostraron una elevada microporosidad, mientras que los materiales obtenidos sin utilizar BP mostraron una mayor contribución mesoporosa. Estos materiales se utilizaron como precursores para preparar catalizadores heterogéneos confinados mediante la coordinación de acetato de paladio(II). Dichos catalizadores se estudiaron en reacciones de acoplamiento cruzado Suzuki-Miyaura utilizando disolventes verdes y condiciones aeróbicas, mostrando excelentes conversiones. Además, estos catalizadores pudieron reciclarse durante al menos cinco ciclos sin pérdida de actividad catalítica ni *leaching*.

Articles included in this Compendium Thesis

Chapter I

L. Matesanz-Niño, N. Esteban, M.T. Webb, A. Martínez-Gómez, F. Suárez-García, A. González-Ortega, J.A. Miguel, L. Palacio, M. Galizia, C. Álvarez, Á.E. Lozano, Polymer Materials Derived from the S_EAr Reaction for Gas Separation Applications, Polymer (Guildf). 267 (2023) 125647.

DOI: 10.1016/j.polymer.2022.125647.

Chapter II

N. Esteban, M.L. Ferrer, C.O. Ania, J.G. de la Campa, Á.E. Lozano, C. Álvarez, J.A. Miguel, Porous Organic Polymers Containing Active Metal Centers for Suzuki–Miyaura Heterocoupling Reactions, ACS Appl. Mater. Interfaces. 12 (2020) 56974–56986.

DOI: 10.1021/acsami.0c16184.

Chapter III

N. Esteban, M. Claros, C. Álvarez, Á.E. Lozano, C. Bartolomé, J.M. Martínez-Ilarduya, J.A. Miguel, Palladium Catalysts Supported in Microporous Phosphine Polymer Networks, Polymers (Basel). 15 (2023) 4143.

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Other publications developed during the PhD not included in this Compendium Thesis

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DOI: 10.1016/j.mtchem.2022.100966

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DOI: 10.1021/acs.joc.3c02069

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DO: I10.1021/acs.iecr.3c04120

Abbreviations

135TPB 1,3,5-Triphenylbenzene

2D Two dimensional

3D Three dimensional

BET Brunauer-Emmett-Teller

BP Biphenyl

CMP Conjugated Microporous Polymer

COF Covalent Organic Framework

CTF Covalent Triazine Frameworks

DCE 1,2-Dichloroethane

DCM Dichloromethane

DF 4,5-Diazafluoren-9-one

DMAc Dimethylacetamide

DMF Dimethylformamide

DMM Dimethoxymethane

DMSO Dimethyl sulfoxide

DPPB 1,4-Bis(diphenylphosphino)butane

DPPE 1,2-Bis(diphenylphosphino)ethane

DPPP 1,3-Bis(diphenylphosphino)propane

DSC Differential scanning calorimetry

EWG Electron-withdrawing group

FB Fluorobenzene

FTIR Fourier transform infrared spectroscopy

GC Gas cromatography

GDP Global gross domestic product

HCP Hyper-crosslinker Polymer

IS 2,3-Indolinedione, Isatin

IUPAC International Union of Pure and Applied Chemistry

LP Linear Polymer

MeIS 1-Methylisatin, N-Methylindoline-2,3-dione

MMM Mixed Matrix Membrane

MOF Metal Organic Framework

MSA Methanesulfonic acid

NMR Nuclear magnetic resonance

NPs Nanoparticles

NZE Net Zero Emmisions

PAF Porous Aromatic Framework

PHADO 1,10-Phenanthroline-5,6-dione

Phen 1, 10- Phenantroline

PIM Polymer of Intrinsic Microporosity

POP Porous Organic Polymer

PPN Porous Polymer Network

SEM Scanning Electron Microscopy

TFA Trifluoroacetic acid

TFSA Trifluoromethanesulfonic acid

THF Tetrahydrofurane

TPP Triphenylphosphine

TRP Triptycene

UV Ultraviolet

WAXS Wide Angle X-ray Scattering

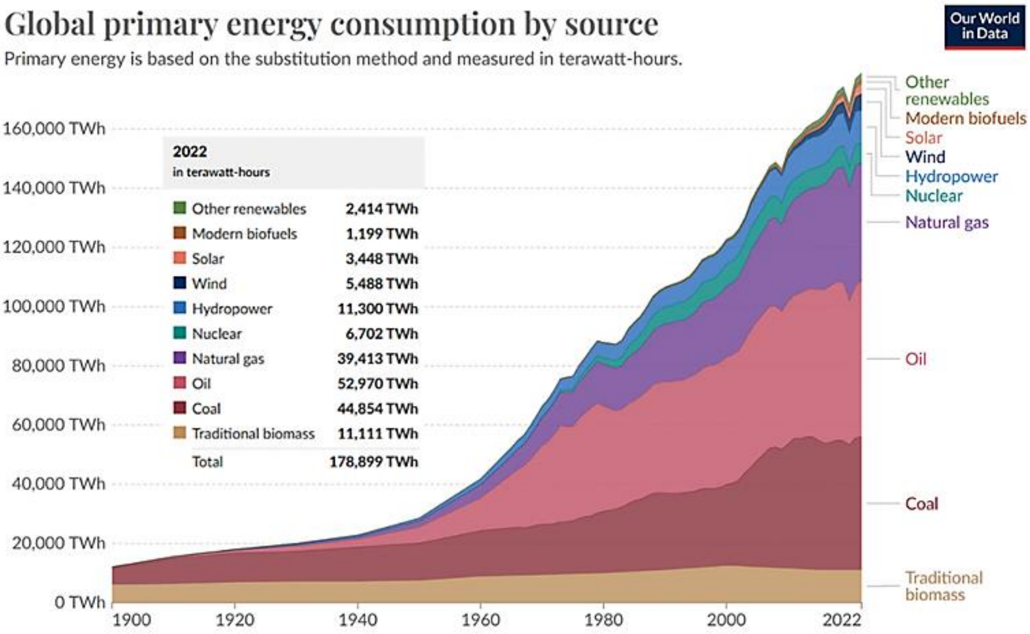
XPS X-Ray Photoelectron Spectroscopy

ZIF Zeolitic Imidazolate Framework

Introduction

1. Energy and catalysis

Since the advent of the Industrial Revolution, there has been a correlation between energy consumption and industrial and economic development. In this context, since the middle of the 20th century, there has been an enormous increase in the consumption of fossil fuels, which are still the main energy sources, accounting for about 80% of total consumption. However, fossil fuels release large amounts of carbon dioxide, leading to a pernicious global environmental situation known as global warming.[1–6] Recently, with the idea of reducing global warming, specifically in the context of limiting the global average temperature to 2 °C above pre-industrial levels and achieving Net-Zero-Emission (NZE) by 2050, the Paris Climate Agreement was established on the 4th of November in 2016. This agreement is a legally binding international treaty signed by 193 countries plus the European Union, which requires the reduction of energy consumption and the immediate use of available clean energy technologies such as wind, photovoltaic, thermo-solar, geothermal, and biomass, instead of fossil fuel sources to achieve a gradual reduction of carbon emissions into the atmosphere, which is known as decarbonization. Figure 1 shows a graphic with the evolution of the global energy consumption of different sources from 1900 to 2022.[7–11]



Data source: Energy Institute - Statistical Review of World Energy (2023); Smil (2017) OurWorldInData.org/energy | CC BY
Note: In the absence of more recent data, traditional biomass is assumed constant since 2015.

***Figure 1**. Global primary energy consumption by source* [12]

Industrial processes accounted for an important percentage of global energy usage. According to data published by the International Energy Agency (IEA),[13] in 2022, the industrial sector was responsible of 37% ($166 \cdot 10^{18}$ J) of global energy consumption, in addition to the emission of 9.0 Gt of CO_2. For this reason, to make progress in decarbonization is imperative to redesign industrial processes, looking for technologies that provide greater efficiency and energy savings, thus reducing the environmental and economic impact.[3,6,14–19]

Among the multiple actions to increase energy efficiency, improvements of catalytic technologies play an important role because catalysts are present in most industrial processes. Catalysts are materials that influence the reaction rate or the direction of chemical processes, improving the selectivity and the efficiency of reactions, allowing to obtain more product in less time or using milder conditions generating less waste, achieving more efficient and sustainable processes. Such is the importance of catalysis in society that catalytic methodologies contribute 35% to the global gross domestic product (GDP), with catalytic processes accounting for more than 80% of manufactured products. In 2023, the global catalyst market was valued at more than USD 20.6 billion.[20] Moreover, catalysts are also used in energy production, for instance, processing crude oil to produce cleaner fuels with low sulfur and nitrogen content or in the production of hydrogen from water, as well as in environment protection processes such as the reduction of nitrogen oxide emissions from stationary sources, in the destruction of pesticides, furans, and dioxins, the carbon dioxide transformation, in the soil decontamination, in the reduction of ozone pollution or pollutants in water, etc.[3,6,28–35,18,21–27]

The importance of catalysis has led to a high level of research and development effort, which has resulted in numerous investigations leading to more than 15 Nobel Prizes. For instance in the area of Chemistry, in 2001, Knowles, Noyori, and Sharpless were awarded for the development of selective and versatile catalysts for the efficient production of pure enantiomers;[36] in 2010, Heck, Negishi, and Suzuki for their contribution in the field of palladium-catalyzed cross-coupling;[37] and more recently, in 2021, List and MacMillan, who developed asymmetric organocatalysis in 2000, were awarded for this new and precise tool for molecular construction.[5,22,38,39]

Besides these three examples of advances in catalysis, there are several catalytic reactions widely used in the industry, for example, the oxidation and reduction reactions, the Lewis acid catalysis reactions, and other photocatalysis reactions and coupling reactions. These last ones, due to their ability to form a wide variety of new bonds (carbon-carbon, carbon-nitrogen, and carbon-oxygen), are very powerful tools in synthesis. Cross-coupling processes have taken great importance in 20th-century organic chemistry, being carbon-carbon (C–C) cross-coupling reaction one of the most studied and useful methodologies to synthesize numerous high-value-added products. In fact, in the last decade, these reactions have awakened great interest at industrial, and academic levels, appearing in numerous publications and patents. Through this type of reaction, usually catalyzed by metals, new C(sp^2)–C(sp^2), C(sp^2)–C(sp^3), or C(sp^2)–C(sp) bonds are formed in a single step. Figure 2 shows some of the best-known C–C coupling reactions.[40–43]

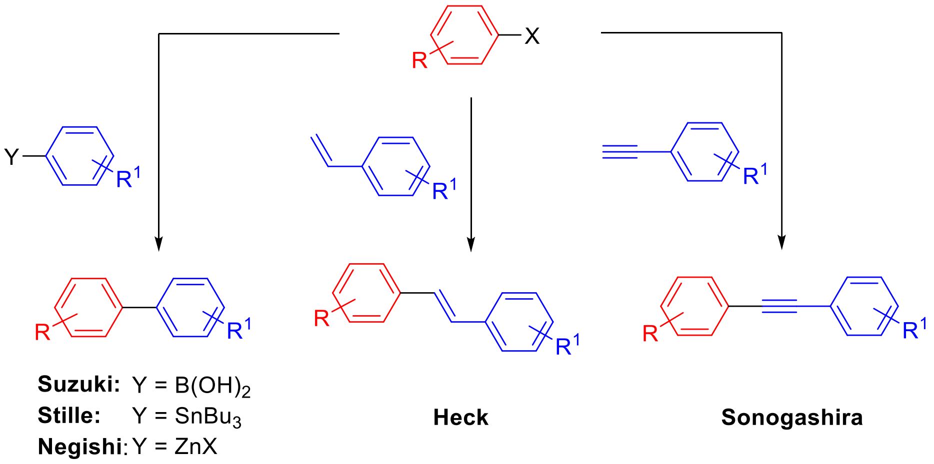


Figure 2. *Typical C–C hetero-coupling reactions*

The Suzuki-Miyaura cross-coupling process is a metal-catalyzed reaction for forming C(sp^2)–C(sp^2) bonds, which occurs between an electrophile (usually an aryl halide) and a nucleophile (commonly a boronic acid), in presence of a base (usually carbonates or phosphates) and using an adequate solvent (for example, DMF, THF, ethanol or toluene). During the reaction, the skeletons of the electrophile and the nucleophile are united as is shown in Figure 3. The availability of common nucleophiles used in this reaction, the usage of mild conditions, and the use of environmentally friendly and less toxic reactants make Suzuki-Miyaura one of the most important reactions in the chemical industry, and, by far, more widely used than other cross-coupling reactions.[44,45]

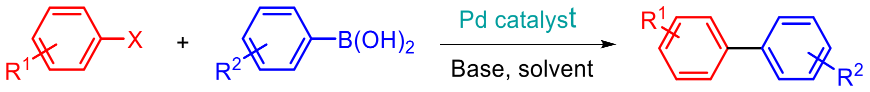


Figure 3. *General scheme of Suzuki-Miyaura cross-coupling reaction catalyzed by palladium*

In conclusion, due to their versatility, this reaction is used in many carbon-carbon bond-forming organic synthesis reactions, mainly in biaryl synthesis, in the obtention of pharmaceutical compounds, polymers, agrochemicals, functional materials, and natural products. Regarding the transition metals used in this reaction (nickel, gold, cobalt, rhodium, iron, copper), palladium is preferred due to its excellent chemical properties and reproducibility, the formation of easily removable bi-products, the wide functional group tolerance and the possibility of using mild reaction conditions.[46–53]

Catalysts are commonly classified into two main groups: homogeneous and heterogeneous catalysts. Homogeneous catalysts are chemical systems in which the catalyst is in the same phase as the reaction medium. These catalysts are quite active and show high selectivities, but present some drawbacks, such as the difficult separation from the reaction medium. Despite this, they are still used in various important chemical processes. Efficient separation of the catalyst from the reaction mixture minimizes contamination of the final products and simplifies the purification process, in which is estimated that almost half of the total energy of the catalytic process is consumed. Heterogeneous catalysts, which are in a different phase than the reaction medium, overcome this disadvantage associated with homogeneous catalysts; however, they usually show lower activity and selectivity. For these reasons, finding catalysts that combine the ideal characteristics of homogeneous and heterogeneous catalysts (tunable activity and selectivity, stability, and recyclability) is the holy grail of catalysis research and a basic requirement for the development of improved green and sustainable chemistry processes.[21,25,59,60,26–28,54–58]

Another method of classification of catalysts is based on the nature of the active catalytic center. The catalytic center may be inorganic, as in many zeolites, or organic (although other atoms may be present such as sulfur, phosphorus, etc). Metallic catalyst is another important subgroup, in which a metal complexed to a ligand, usually organic, produces the catalytic activity. Among them, organotransition metal catalysts have occupied a privileged position due to their ability to navigate between different oxidation states and coordination numbers during the catalytic cycle. In addition to this, the properties of the active site can be easily tuned through rational modification of the ligands to achieve good selectivities and activities. Although noble metal-based organometallic catalysts remain at the forefront, many recent advances based on earth-abundant analogs have been developed.[61,62]

Within the heterogeneous catalysts, a series of new catalysts have been developed that have aroused enormous academic interest in recent years, since they have the ability to modify reaction rates in a manner similar to those observed in the active center of enzymes. These materials are the so-called confined catalysts. The concept of confined catalyst refers to the assembly of an active molecule within the fractional free volume units (pores) of a material. The assembly is crucial and must meet some requirements such as a suitable cavity for the anchored catalyst, good anchoring to avoid possible leaching of the active molecules, adequate pore size and pore distribution to allow transport of substrates and stability of pore structure and the catalyst. Confinement has been shown to improve catalytic performance by modifying the physicochemical properties of the reactant molecules, such as adsorption energy, and often prolongs the lifetime of the reactants and reaction intermediates on the catalyst surfaces, which improves reaction performance. In addition, confined spaces can modulate selectivity and tune catalytic reactions.[23,34,58,63–69]

Finally, in other classifications electrocatalysts, and photocatalysts are considered catalyst subtypes.[35,70] In electrocatalytic processes, the use of a catalytic entity and the application of a differential potential at the electrode/electrolyte interface modify the reaction rate. These systems can be applied in energy conversion and storage or electrochemical water treatment. In photocatalytic materials, the reaction rate is modified under radiation energy (UV, visible, or IR) in the presence of a photoactive catalyst, e.g. titanium dioxide, which can oxidize the organic matter for applications such as waste-water treatment and water disinfection, or in self-cleaning glass or self-sterilizing applications based on photocatalytic coatings.[35,71]

2. Porous materials used as catalytic supports

Porous materials play an important role in the academic and industrial world due to their interesting properties, which make them useful for multiple applications, including catalysis. There are a multitude of porous materials of different natures (inorganic, organic, hybrid, etc.) that can anchor catalytic systems within their structure. In this doctoral research report, porous polymeric materials, particularly microporous ones, have been developed and used for their use as heterogeneous catalysts. Therefore, the more specific characteristics of a polymeric material will be introduced by defining these systems.

Polymers are very large molecules formed by a chemical combination of different repeat molecules called monomers.[72,73] Over the years, several classifications of polymers have been published, for example, they can be classified based on their origin (natural, synthetic, or semi-synthetic polymers); their structure (linear polymers, branched polymers, or crosslinked polymers); according to their structural and chemical composition (inorganic, organic or hybrid polymers) or attending to other features (elastomers, thermoplastics, thermosetting plastics or fibers).[73–76] In 1931, Carothers made the first polymer classification,[77] differentiating polymers into two main groups: Addition or chain-growth polymers, and condensation or step-growth polymers.[72,77] Chain polymerization involves the successive addition of monomer molecules to an activated intermediate (usually radicals or ions), and it consists of three stages (initiation, propagation, and termination). Step-growth polymerization consists of the reaction between monomer molecules with two or more reactive groups. These polymers are formed by sequenced condensation reactions, in which an element (hydrogen, nitrogen…) or a small molecule, generally water, is liberated as a subproduct. When the polymerization reaction takes place between monomers having more than two reactive groups (average monomer functionality higher than two), the reaction leads to a crosslinked polymer (polymer network).

Porous polymers could be linear or crosslinked polymers. According to the pore classification recommended by IUPAC in 1985, porous polymers can be sorted into three main groups: macroporous polymers, which are materials with pores diameters higher than 50 nm; mesoporous polymers, which are materials with porous diameters between 2 and 50 nm; and microporous polymers, which are materials with a porous diameter smaller than 2 nm.[78] The internal features of these porous materials are usually determined by gas adsorption, and the presence of microporous in a material gives very high specific surfaces, while on the other side, when dealing with a macroporous material the specific surface areas are low. Commonly, the Brunauer-Emmett-Teller (BET) method[79] is applied to determine this specific surface area of porous materials, crystalline or amorphous, based on nitrogen adsorption/desorption isotherm measurements at 77 K (boiling temperature of nitrogen). When the material shows very small and narrow microporous, it is better to determine the pore size distribution (PSD) using other adsorbates such as argon or carbon dioxide, which also makes it possible to determine the specific surfaces at different temperatures.[80–82]

Porous polymers can be designed and obtained through multiple methodologies. It should be noted that each synthetic methodology will cause their properties (structure and pore size) and applications to be different. Among the many applications of these porous polymeric materials are heterogeneous catalysis, ion exchange, supercapacitors and batteries, water purification, CO_2 conversion, adsorption, separation and storage of gases, and photovoltaic applications. Therefore, the development of new porous polymers with high porosity has become of great interest not only at the scientific but also at the industrial level.[59,83,92–95,84–91]

Regarding catalytic processes, since the 1960s, some catalysts, immobilized in different porous supports, have been utilized and reported. Although porous polymers seem to be the most interesting option to be used as support in heterogeneous catalysis, other porous materials have been used as support in this field for years. The classification of these porous materials is ambiguous in the bibliography, in Figure 4 is displayed a classification in which porous polymers are included. In this classification, polymers of intrinsic microporosity (PIMs), which are mostly linear polymers rather than networks, have been included in the group of porous organic materials because they exhibit intrinsic microporosity.[87,96,97]

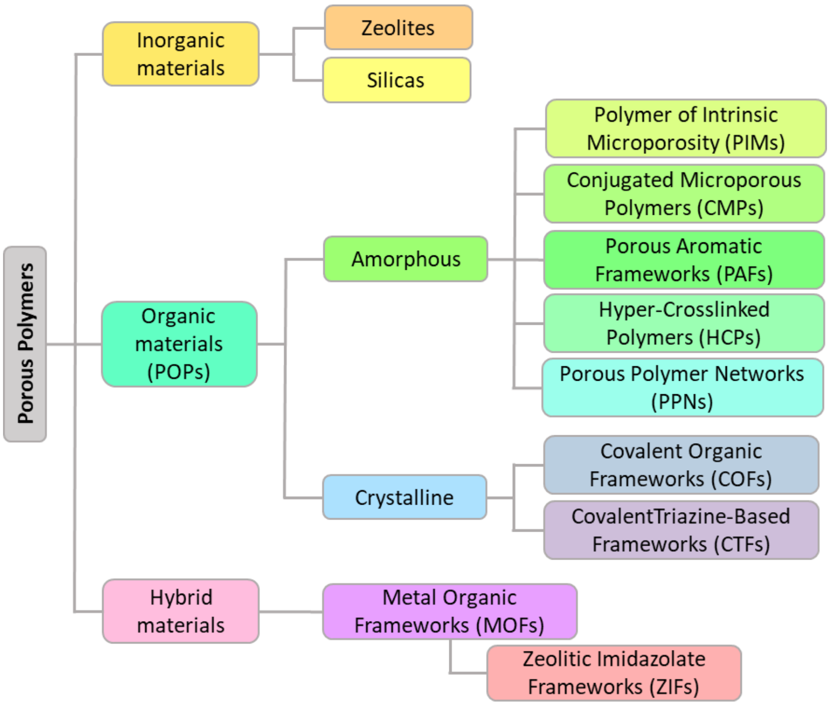


Figure 4. *Porous materials classification*

Ones of the first materials used as supports in catalysis were polymer resins, which are polymer networks (crosslinked polymers). In these materials, the use of a suitable solvent, which swells the material, is one of the keys to its effectiveness as a catalyst. Merrifield-type resins are commercial resins derived from polystyrene polymers that remain one of the most popular polymeric materials studied for their use as heterogeneous catalyst supports, mainly in the chemical and petrochemical industries. In general, these resins possess groups that allow them to be easily chemically modified and have adequate chemical and mechanical stabilities. However, these resins have drawbacks such as low surface area, which limits the accessibility of the reagents to the active sites, reducing catalytic efficiency. Therefore, the search for materials that can overcome these drawbacks is crucial.[39,98–104]

Zeolites are crystalline aluminosilicates with three-dimensional (3D) structures, showing micro and mesoporous with selective size and shape. These inorganic materials are widely used as catalysts in the industry, especially for petrochemistry (cracking, production of oxygenates and hydrocarbons, hydrocracking…), oil refining, and organic synthesis. Their features such as very high surface areas, adsorption capacity, active sites, or the appropriate size of their channels and cavities make them interesting to be used as heterogeneous catalysts. In addition, zeolites can be activated to produce materials with high thermal and chemical stabilities.[24,67,105–107]

Porous silicas are inorganic porous materials that are chemically and thermally stable, with uniform pore size and distribution, high surface area, and high adsorption capacity. These materials are frequently used as inorganic support with the target of immobilizing metal particles that show a catalytic behavior. However, these materials are easily hydrolyzed in alkaline media and show poor adsorption selectivity.[108–111]

In the group of hybrid materials, Metal-Organic Frameworks (MOFs) stand out. Their structures are formed by metal ions and organic multidentate ligands (linkers) connected by coordinating (ionic) bonds. These materials, designed and successfully synthesized by Yaghi and coworkers in 1995,[112] are crystalline 3D materials having a regular and symmetrical disposition. Due to their medium-high thermal stability, their high density of surface sites, and the possibility of being reused, MOFs are fascinating materials to be used as support in heterogeneous catalysis. Usually, these materials show higher BET surface areas and pore volume than conventional crystalline microporous inorganic materials, such as zeolites. However, MOFs show inherent defects that limit their application scope. A possibility to solve these limitations is to prepare composites combining MOFs with other functional materials. Thus, zeolitic imidazole frameworks (ZIFs), a subtype of MOFs, are materials composed of tetrahedrally coordinated metal ions connected by organic imidazole ligands, are considered.[58,106,113–119]

Porous Organic Material Polymers (POPs) are obtained from organic monomers using different polycondensation synthetic strategies such as nucleophilic substitution reactions, Friedel-Crafts alkylation reactions, or other coupling reactions. These materials are an interesting alternative to inorganic supports. The powerful features of these polymer materials (high specific surface areas, adjustable pore volume and distribution, thermal, chemical, and physical stability, and synthetic diversity), added to the feasibility of having adequate functional groups in their structures, make them suitable candidates as support materials to be applied in the synthesis of heterogeneous catalysis. When these organic materials are modified by introducing metals into the structure it could be said that they become hybrid materials.[83,120,121]

POPs can be divided into two main groups, crystalline and amorphous materials. Within the crystalline POPs, Covalent Organic Frameworks (COFs), reported in 2005 by Yaghi and coworkers,[122] are the most outstanding. The first COFs were designed and successfully synthesized by condensation reactions between phenylboronic acid and hexahydroxytriphenylene, resulting in two-dimensional (2D) or 3D ordered crystalline microporous polymers with accessible channels, which show high chemical and thermal stabilities, large BET surface area, and when well-designed can anchor active metals such as Pd, Pt, Cu, Ag, and Au or can immobilize other catalytically active species. The great amount of toxic solvent used in the solvothermal synthesizing method of COFs is a highlighted disadvantage of these materials, thus, is necessary to find greener synthetic methods.[83,106,123–125]

Covalent Triazine-Based Frameworks (CTFs), which are formed by strong covalent aromatic C=N linkage (triazine units) without weak bonds in their structure, are other interesting materials in the group of crystalline POPs introduced in 2008 by Thomas and coworkers.[126] CTFs are stable materials with high nitrogen content and high BET surface areas. Among their multiple applications, these materials have been used in photocatalysis and heterogeneous catalysis, for example in the production of hydrogen from formic acid or the ammonia decomposition process. Nowadays, with the advances in their research, these materials, in some cases, are also classified as amorphous POPs instead of crystalline ones.[127–129]

Amorphous POPs despite not having crystalline order, are interesting candidates for heterogeneous catalyst supports because they have tunable porous sizes, high surface areas, robust architecture, and chemical functionalities. Additionally, these polymers can stand vigorous post-treatments to modify their cavities or their functionalities.[58,81,121]

As discussed above, in some classifications PIMs are not included as POPs because most of them are linear polymers instead of networks, however, these polymers show intrinsic microporosity in their structures due to their ladder backbones with highly rigid and contorted molecular structures that result in defined interconnected micropores. These materials, introduced in 2006 by McKeown and Budd research groups,[130,131] show features like high microporosities, high surface areas, good chemical and thermal stability, and good processability that make them interesting candidates for applications such as hydrogen storage, gas separation or heterogeneous catalysis. However, the synthesis of monomers employed to prepare PIMs is multistep and the polymerization process is cumbersome, which hinders their application in industry.[30,132–136]

Another representative amorphous POPs widely used as heterogeneous catalysts are the Conjugated Microporous Materials (CMPs), which were reported for the first time in 2007 and were synthesized by using the Sonogashira-Hagihara cross-coupling reaction.[137] The control of functionality and structure of these CMPs is due to the large variety of monomers that can be used in the multiple coupling reactions that are used as synthetic routes, being able to have 2D or 3D structures. These materials formed by a π-conjugated skeleton show mechanical rigidity, and optoelectronic properties, and are easily tunable. Additionally, CMPs have permanent microporosity and show high chemical and thermal stability as well as high specific surface area.[138–142] Polymer Aromatic Frameworks (PAFs), reported for the first time in 2009 by Zhu and coworkers, show many similarities with CMPs.[143] PAFs are built by C-C linked aromatics units, usually *via* Yamamoto coupling, producing polymers with a rigid skeleton, exceptional surface areas, high capacity uptake for carbon dioxide and hydrogen, hydrophobicity, and thermal stability. Due to their tunable structure, these materials can be used for several applications, including heterogeneous catalysis.[144–147]

3. State-of-art and approach

Looking at the interesting properties of amorphous POPs, new network materials were recently developed in our research group by using the hydroxyalkylation, S_EAr, reaction,[148] which are based on the super electrophilic substitution methodology proposed by Olah *et al.* and on the work about linear polymers (LPs) by the Zolotukhin's group.[149] These highly cross-linked systems are a type of Porous Polymer Networks (PPNs), though in this research work these materials will be called by the acronym of the general group POP.

In 1975,[150] Olah introduced the concept of superelectrophiles, compounds whose reactivity is far superior to that of other electrophiles. These reagents are electrophiles with a doubly electron deficient nature that can be activated by interaction with Bronsted or Lewis acids.[151,152] For instance, the presence of an electron-withdrawing group (EWG) can significantly increase the electrophilic reactivity of carbonyl groups and their protonated carboxonium ions. As shown in Figure 5, whereas in super acidic conditions, the protonated acetophenone is unreactive with weak π-nucleophiles (for example benzene), a ketone or aldehyde activated by an EWG can undergo successive condensation reactions with weaker nucleophiles, even with deactivated aromatic rings, due to a super reactive intermediate (super-electrophile), which is formed after a protonation step.[151,153]

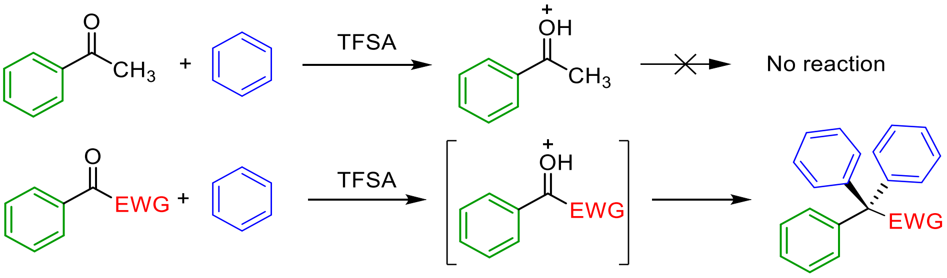


Figure 5. *Scheme of the different reactivity between deactivated and activated ketones*

In 2001, Zolotukhin and coworkers published the first application of this chemistry in polymer synthesis, publishing new aromatic polymers; polyaryleneoxindoles. These polymers were synthesized by reacting polynuclear aromatics (e.g., biphenyl (BP), p-terphenyl (pTP), or diphenyl ether) with equimolar quantities of isatin (IS) in a strong acidic media, trifluoromethanesulfonic acid (TFSA) solution, at room temperature. These polymers showed high glass transition temperatures (T_g) and high molecular weights.[149] A general scheme of these polymer reactions is shown in Figure 6. Using this methodology, several linear polymers were synthesized by a one-pot superacid catalyzed reaction using different acid media, for instance, using a Brønsted superacid (TFSA), or a mixture of TFSA with methanesulfonic acid (MSA), and/or trifluoroacetic acid (TFA). According to the molecular weight of these polymers, it was demonstrated that the polymer-forming reaction is greatly dependent on the medium acidity.[154–157]

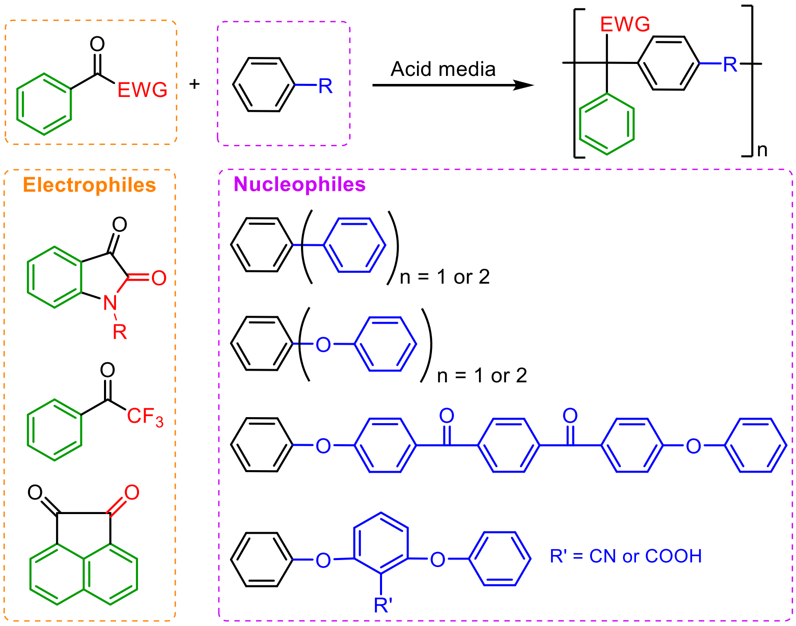


Figure 6. *Scheme of linear polymers synthesis proposed by Zolotukhin and coworkers and some examples of monomers used*

With this knowledge, in 2018, our research group reported a family of amorphous porous polymer networks, which were synthesized by reacting two activated ketones by an electron-withdrawing group (IS and TFAP) as difunctional monomers, with a rigid three-functional aromatic monomer (triptycene, TRP, or 1,3,5-triphenylbenzene, 135TPB) in an acidic media, using TFSA as promotor acid and chloroform as cosolvent. Figure 7 shows a simplified scheme of the synthesis of these network materials.[148]

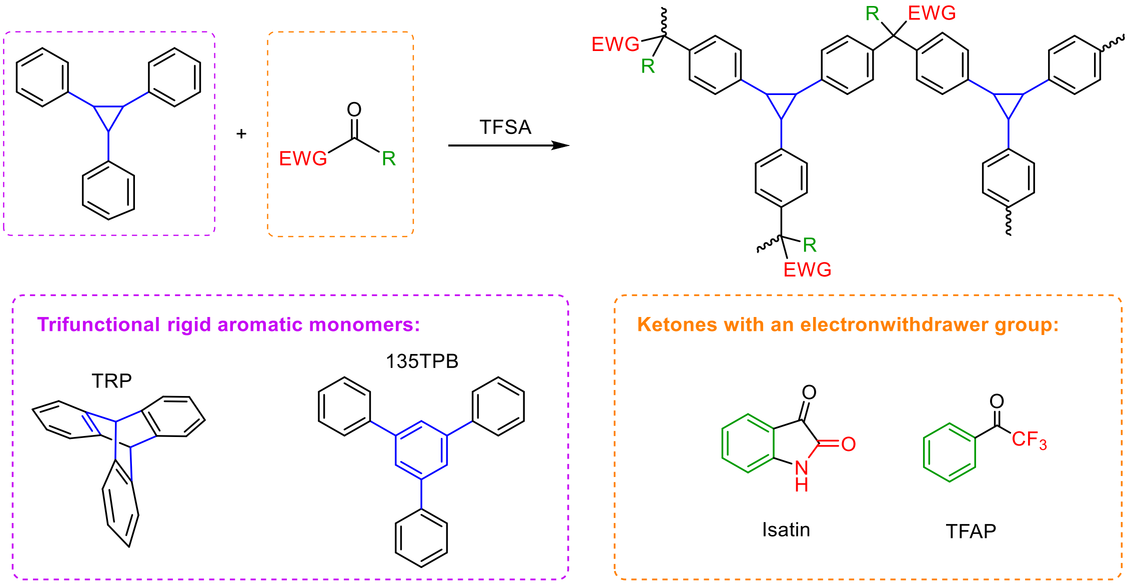


Figure 7. *Simplified scheme of the synthesis of porous polymer networks by S_EAr using TFSA as promotor acid developed in our research group*

These novel microporous materials showed moderate-high Brunauer-Emmet-Teller (BET) specific surface areas between 580 and 790 m^2/g and high thermal stability, above 420 °C. Due to the presence of a lactam group, the materials containing IS in their structures, a good chemical interaction with CO_2 was observed, and they showed excellent results in CO_2 uptake (up to 207 mg g^{-1} at 0 °C and 1 bar).[148] These POPs were used as fillers in mixed matrix membranes (MMMs), particularly using the polymer network TRP-Isatin (2:3), observing good compatibilities between the polymer matrix and the POP.[158] Furthermore, several MMMs were prepared using these POPs as filler, inclusive by using thermally rearranged (TR) polymeric matrixes. These MMMs were studied in gas separation applications with different gases, observing improvements in the permeability-selectivity ratio.[158–162] Figure 8 displays the Robeson plot of the permeability vs. selectivity results for the CO_2/CH_4 gas mixture separation of the MMMs prepared using the POPs of this Ph.D. memory. Robeson plot is a graph, used to quantify gas separation productivity, where the permeability to the most permeable gas of a mixture is plotted against the selectivity of that mixture. In gas separation processes, the performance of a membrane depends on permeability (flux across the membrane) and selectivity (the ability of the membrane to discriminate a gas from the other components of the gas mixture), where the two properties are inversely related. This inverse relationship, practically universal, is the main drawback of membranes, compared to other gas purification processes, since when an increase in permeability is achieved, a simultaneous decrease in selectivity is observed. Robeson proposed in 1991, some empirical relationships between permeability and selectivity known as Robeson's boundary conditions (Robeson limits), by evaluating a substantial number of gas mixture pairs (later in 2008, he improved the Robeson limits using the polymer membranes developed up to that date). This upper bound limit represents the limiting value of selectivity that a polymeric membrane with a given permeability can give (more details are explained in the section Properties of Gas Transport). Figure 8 shows the improvements in membrane productivity (proximity to the boundary) when a polymer matrix is combined with POP fillers (this improvement is greater when the percentage of filler is higher).

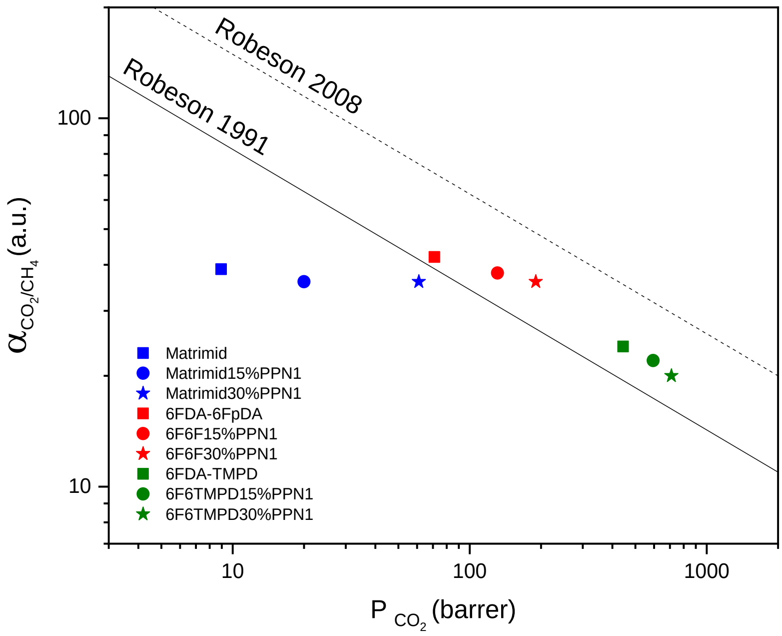


Figure 8. *Robeson plot for CO_2/CH_4 separation. Experimental data from bibliography.[158] The square symbol is the matrix polymer, the circle symbol is the matrix + 15% filler, the triangle symbol is the matrix + 20% filler, and the star symbol is the matrix + 30% filler. The x-axis represents the CO_2 permeability (CO_2 is the most permeable gas of the mixture) and the y-axis is the selectivity (α) for the gas pair CO_2/CH_4.*

In addition to their application as fillers in MMMs, these materials, when are accurately modified, could be used in other applications, for example in heterogeneous catalysis. In 2022, IS-derived COPs, which were modified by derivatization of the lactam unit, afforded confined catalytic materials possessing pyrrolidine moieties. These modified POPs, using mild and sustainable conditions with green solvents, efficiently catalyzed the formation of C=C and C=N bonds, using iminium and enamine activation. This method, free of metal and acids, is scalable and recyclable. Moreover, these heterogeneous catalysts based on pyrrolidine were used efficiently in the Knoevenagel reaction and the preparation of alkenes in aldolic condensation using green solvents. Figure 9 shows a simplified scheme of the POPs syntheses.[163]

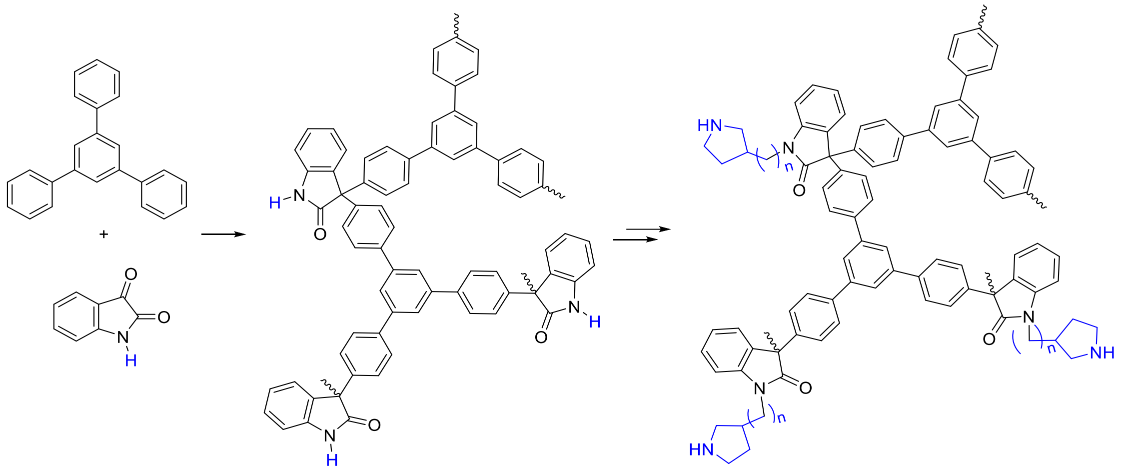


Figure 9. *Simplified scheme of synthesis of heterogeneous catalysts based on pyrrolidine.*

Recently, in our research group other POPs derived from IS were functionalized to give heterogeneous Au(I) carbene catalysts. These new confined carbenes were studied in catalytic tests in the cyclization of a 1,6-enyne, proving to be very active for the skeletal rearrangement of dimethyl 2-(3-methyl-2-butenyl)-2-propinylmalonate enyne. Furthermore, it was observed a large increase in the stability of these heterogeneous Au(I) catalysts when compared to other homogenous catalysts described in the bibliography. A simplified scheme of one of these catalysts is displayed in Figure 10.[164]

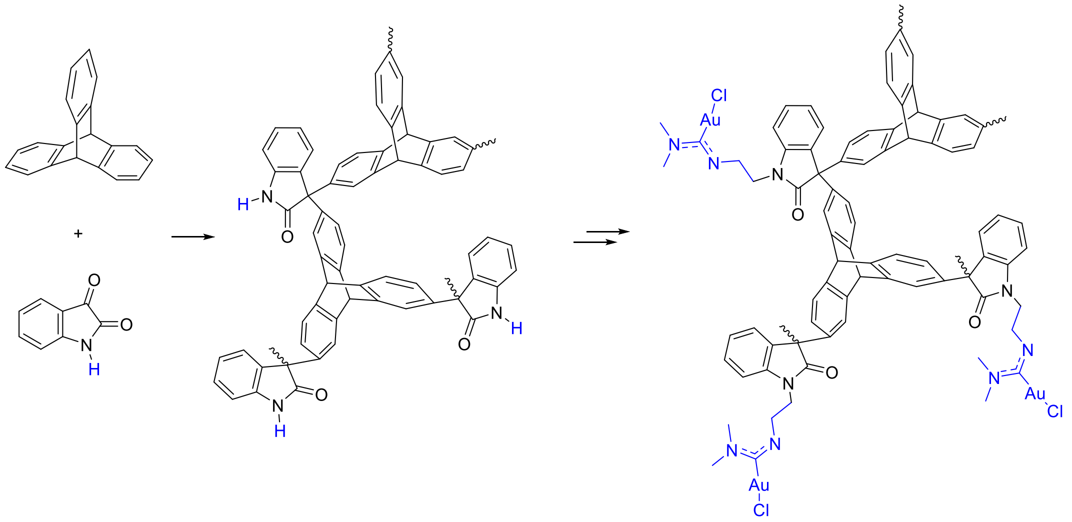


Figure 10. *Simplified scheme of preparation of heterogeneous Au(I) catalyst.*

More recently, a new organocatalyst based on a polymer-supported bifunctional thiourea was reported by our group. The catalyst was prepared by modification of a linear polymer synthesized by reaction of BP and IS in stoichiometric ratios. Then, the hydrogen bonded to the nitrogen in the lactam ring was replaced by a thiourea moiety in a multi-step synthesis. This new compound proved to be an efficient heterogeneous catalyst for enantioselective amination. This catalytic material could be recycled and reused for 6 cycles without any significant loss of activity in batch and for four runs in continuous-flow conditions. Additionally, this catalyst allowed the synthesis of 4-amino-pyrazolone derivatives in a gram scale with high yield and enantioselectivity. The synthesis of this catalyst is shown schematically in Figure 11.[165]

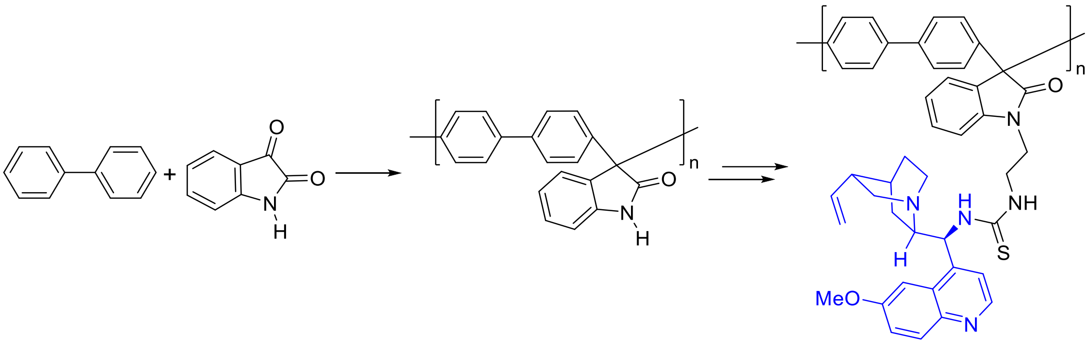


Figure 11. *Simplified scheme of catalyst based on thiourea*

Another SEAr synthesizing strategy to prepare POPs is known as braiding or *knitting*.[166] This methodology is a low-cost and versatile strategy proposed by Tan and co-workers, where a rigid aromatic nucleophile monomer (or a mixture of rigid aromatic nucleophilic monomers) is *braided* by an electrophile, which acts as a linker in the presence of a Lewis acid promotor ($AlCl_3$ or $FeCl_3$) in a one-step Friedel-Craft reaction (Figure 12). By this methodology, microporous hyper-crosslinked polymers (HCPs) also called *knitting* aromatic polymers (KAPs) were obtained.

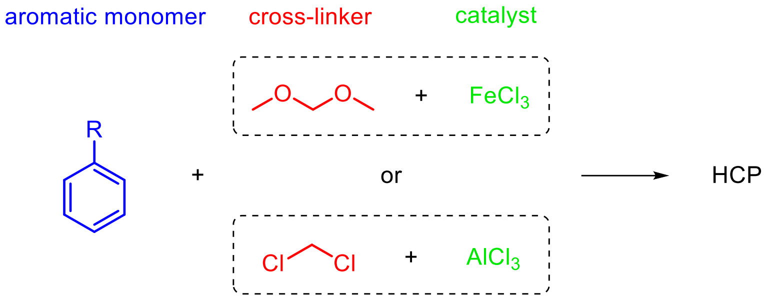


Figure 12. *General scheme of knitting synthetic strategy*

The first series of these HCPs, published in 2011, were synthesized by reacting a rigid aromatic building block (benzene, BP, 135TPB, methylbenzene, chlorobenzene, and phenol) with dimethoxymethane (DMM) as an external crosslinker, iron(III) chloride as the acid catalyst and dichloroethane as solvent. These materials showed BET surface areas between 400 and 1400 m^2/g and CO_2 adsorption capacity higher than 15.9 wt%. The structural characteristics of these porous materials, e.g. high surface area, give them potential applications in separation, gas storage, and heterogeneous catalysis.[166]

Since 1980, triphenylphosphine (TPP), due to its low cost and catalytic efficiency, has been used as a ligand in Suzuki-Miyaura cross-coupling reactions catalyzed by palladiums. However, this ligand also shows some limitations such as the high air-sensitivity of its complexes, which makes it difficult to recover and recycle the catalyst. For this reason, the search for more stable heterogeneous catalysts derived from TPP ligands in their structures has been an interesting research subject. In 2012 Tan and coworkers proposed the attainment of copolymers using benzene and TPP as rigid aromatic monomers by employing a *knitting* strategy (Figure 13). The microporous structure of these polymers containing phosphine ligands in their backbone allowed a high dispersion of palladium chloride in their structure. These heterogeneous catalysts exhibited excellent activity and selectivity with aryl chlorides in cross-coupling Suzuki-Miyaura reactions, using mild conditions and an aqueous media.[167] In addition, HCPs with TPP skeleton were successfully used as supports for silver nanoparticles (NPs) because the phosphine structure has a stabilizing effect on these NPs. These HCPs showed potential interest for the fixation of CO_2.[168]

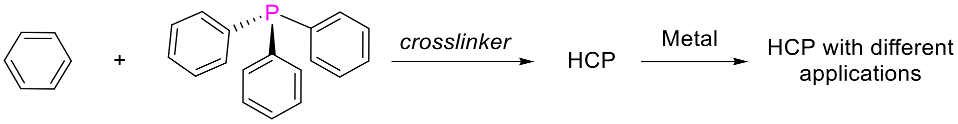


Figure 13. *HCP with triphenylphosphine skeleton*

In 2017, other heterogeneous catalysts prepared by direct *knitting* were published by introducing the metal center (palladium) in the HCP structure directly in the polymerization reaction. This catalyst was prepared by using tetrakis(triphenylphosphine)palladium(0) as the main building monomer (Figure 14(a)) and benzene as a comonomer through a Friedel-Craft coupling reaction. Thus, the unstable homogenous catalyst $Pd(PPh_3)_4$ could be immobilized, stabilized, and dispersed inside the tridimensional microporous polymer structure. These heterogeneous catalysts presented excellent activity and selectivity in C–C bond formation reactions, in the Suzuki-Miyaura reactions between aryl chlorides and alkyl boronic acids, in reductive and oxidative biaryl synthesis in aqueous media, and in C–H regioselective activation/functionalization reactions. Moreover, these heterogeneous catalysts could be easily recovered and recycled without metal leakage or decreased activity.[169]

In 2019, an HCP synthesized by *knitting* copolymerization of TPP with benzene as matrix polymers, an HCP-TPP-Ru(III) precursor for hydrogen evolution reaction (HER) and ammonia borane hydrolysis was obtained.[170] In the same year, new metal-based HCPs using TPP complexed with ruthenium, and gold (Figure 14(b)), were *knitted* and studied as heterogeneous catalysts. Ru-based HCPs were effective for the synthesis of imines, whereas Au-based HCPs were effective for the hydration of alkynes.[171]

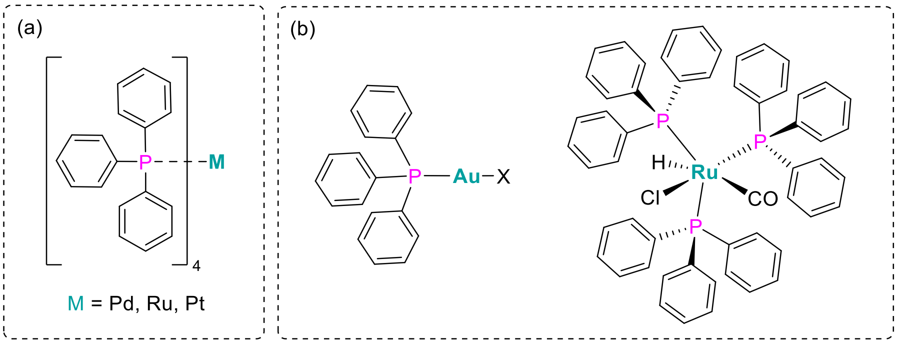


Figure 14. *Metallic monomer precursors of HCP heterogeneous catalysts*

In the last decade, several aromatic monomers, in addition to TPP and benzene, have been used as nucleophiles in *knitting* synthetic methodology, Figure 15 shows some of these monomers used in the bibliography to prepare HCPs.[172–180]

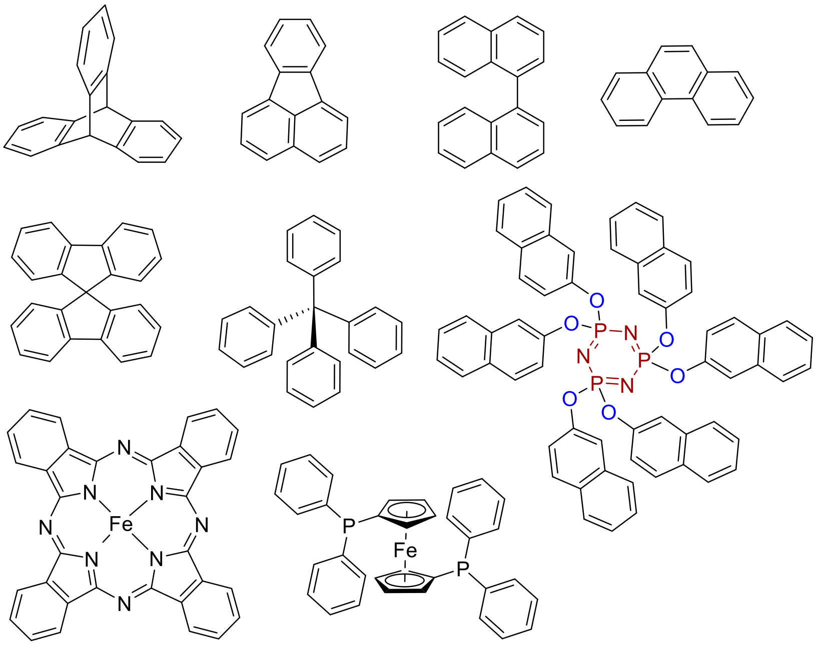


Figure 15. *Monomers used in the synthesis of new knitting aromatic polymers*

In 2020, heterogeneous catalysts were reported by dispersion of palladium chloride into HCPs. These HCPs were prepared by external crosslinking of 1,2,3-triazol and benzene with DMM. These heterogeneous catalysts were highly active for the Suzuki-Miyaura coupling reaction and could be reused six times without important loss of catalytic activity.[181] In the same year, it was reported a heterogeneous catalyst synthesized by supporting palladium nanoparticles (Pd-NPs) into an HCP prepared by crosslinking pyrene with 1,10-phenanthroline using DMM as the crosslinker. The high porosity of the material and the phenanthroline skeleton improved the stability of the Pd-NPs. This catalyst showed excellent catalytic activity and selectivity in the aerobic oxidation of alcohols and was reused five times without loss of catalytic activity.[182]

In the last two decades, several HCPs have been published, using different aromatic monomers, not only in catalytic applications but also in other applications such as CO_2 storage.[172–180] Additionally, this synthetic strategy has been used to increase the surface area by post-*knitting* CMPs, improving its CO_2 adsorption capacity.[139]

Approach and thematic relationships between Ph. D. research works (Journal publications)

In this PhD thesis, heterogeneous confined metal catalysts were obtained by including palladium(II) salts in different porous polymer networks (POPs). The catalytic activity of these materials was tested for C–C cross-coupling reactions.

These catalysts have the catalytic center confined inside of microporous polymeric networks, which were obtained from monomers that have centers capable of forming complexes with metals. For their design, rigid aromatic monomers with N or P atoms were selected, so that after the introduction of a metal in their structure, these POPs could be used as high-performance heterogeneous catalysts. In our case, palladium(II) cations were the selected metal due to their partially filled d orbitals tend to work synergistically with the excess electrons from N and P atoms resulting in the formation of heterogeneous catalysts with higher activity and longer life. Thus, to accomplish this target, a monomer, possessing a bipyridine group, specifically, 4,5-diazafluoren-9-one (DF), was obtained. Also, a series of aromatic commercial diphosphines; 1,2-bis(diphenylphosphino)ethane (DPPE), 1,3-bis(diphenylphosphino)propane (DPPP) and 1,4-bis(diphenylphosphino)butane (DPPB) were selected as monomers.

In ***Chapter I***, to gain insight into the feasibility of 4,5-diazafluoren-9-one (DF) as a polycondensation monomer, the differential reactivity of DF was studied, and compared, under hydroxyl alkyl SEAr reaction conditions, with activated ketones having electron-withdrawing groups such as isatin (IS) and N-methylisatin (MeIS), which are known to form polymer materials. Finally, the reactivity of this monomer DF as a polycondensation monomer was studied by synthesizing high molecular weight linear polymers by the hydroxyalkylation reaction using TFSA as an acidic promotor. The polymerization reaction had to be optimized since the methodology described in the literature for making polymers from monomers such as IS, or MeIs, was inadequate to obtain polymers with enough molecular weight due to the low reactivity of the DF monomer. After optimizing the reaction conditions, high molecular weight polymers were obtained from DF. These polymers showed high thermal and chemical stabilities, and they could be processed as membranes, which showed enough good mechanical properties to be studied in gas separation studies.

With this knowledge about the reactivity of DF and its ability to prepare polymers by S_EAr, in ***Chapter II***, a new family of POPs derived from this monomer was obtained. For this new family of POPs, 1,3,5-triphenylbenzene (135TPB) was chosen as a rigid trifunctional aromatic nucleophilic monomer and IS was selected as the electrophilic difunctional comonomer. The synthesis of these POPs was tuned up based on the sought material properties; high reaction yield, large microporosity, and good thermal and chemical stabilities. These materials having bipyridine moieties could coordinate Pd(II), resulting in heterogeneous catalysts. Thus, palladium acetate was anchored to these POPs, and after being characterized, they were studied as catalysts in the Suzuki-Miyaura reaction. The best conditions to use these catalysts in the Suzuki-Miyaura reaction were optimized prioritizing the use of green solvents.

Given the excellent results of these heterogeneous DF-derived catalysts and attending to the literature data on the use of diphosphines as ligands for palladium, in ***Chapter III***, new hypercrosslinked POPs were designed and synthesized using alkyldiphosphines with different alkylic chain lengths between phosphorous atoms to. The consideration of using diphosphines is derived from the fact that in this chemical system two phosphorous atoms are relatively close to each other and can complex metals in a more stable way over time than other catalytic materials (i.e. triaryl phosphines).

First, the reactivity of these diphosphine monomers was studied, and the reaction conditions were optimized to prepare the POPs. The new POPs were synthesized by *knitting* copolymerization of a diphosphine (DPPE, DPPP, or DPPB) with 135TPB, or with a mixture of 135TPB and biphenyl (BP) using dimethoxymethane (DMM) as external the crosslinker and $FeCl_3$ as the Lewis acid promoter. Subsequently, these POPs were treated with palladium acetate, to complex the metal on the phosphorous atoms, resulting in heterogeneous catalysts, which were studied in the Suzuki-Miyaura reaction, showing excellent results. Furthermore, the use of different alkyldiphosphines permitted us to determine how the length of the alkyl chain between the phosphorus atoms influenced the catalytic properties and stability of these materials.

To sum up, different families of heterogeneous catalysts with excellent catalytic properties were synthesized from DF and diphosphines, observing that they could easily be recovered from the reaction mixture, allowing their recyclability. In addition, a family of linear polymers derived from DF was obtained, which showed good gas separation properties.

Aim and Scope of the Thesis

There is a social need to increase social welfare without causing environmental damage or increasing global warming. In this context, the search for much more efficient industrial systems that produce significant savings in terms of energy is a pressing need.

Catalysts are a powerful synthetic tool; used in various industrial processes, that accelerate the reaction rate, resulting in an improvement of the reaction process together with significant energy savings. However, there are several limitations in many of the catalytic systems currently in use, including the difficulty of separating the catalyst from the reaction medium. Therefore, the design and development of new materials that have the catalyst immobilized within their structures should lead to advances demanded by the industry.

Under this objective, the main goal of this doctoral thesis project, entitled *High porosity polymers for advanced applications*, has been to obtain microporous polymeric catalytic network materials, that incorporate a metal atom as the active center of catalysis, and which can be used as high-efficiency heterogeneous catalysts. The specific objectives of this memory were the following:

- Design and selection of suitable monomers to obtain new high microporosity polymeric materials. Thus, monomers having chemical groups capable of metal coordination were chosen and obtained.
- Study of the reactivity of the selected monomers to ensure that they are suitable to undergo high-yield polycondensation processes. In particular, a new difunctional monomer with the ability to form complexes with metals was obtained. In a proof of concept, this monomer gave high molecular weight polymers, which were tested as obtain gas separation membranes.
- Optimization of the polycondensation reaction and synthesis of microporous organic polymers (POPs) containing bipyridine in their structure.
- Optimization of the polycondensation reaction and synthesis of microporous organic polymers (POPs) containing aromatic alkyl diphosphine moieties in their structure.
- Characterization of the POPs by macromolecular techniques.
- Optimization, preparation, and characterization of materials by including palladium(II) cations in the POPs.

- Study of the catalytic activity and recyclability of the confined Pd(II) catalysts obtained by using green and aerobic conditions.
- Study of the scalability of catalytic reactions using these heterogeneous catalysts.
- Writing and publication of results in first quartile (Q1) journals.

Materials

The reagents and solvents used in the synthesis of polymers were 1,3,5-triphenylbenzene (135TPB), triptycene (TRP), biphenyl (BP), isatin (IS), triphenylphosphine (TPP) 1,2-bis(diphenylphosphino)ethane (DPPE), 1,3-bis(diphenylphosphino)propane (DPPP), 1,4-bis(diphenylphosphino)butane (DPPB), iron(III) chloride anhydrous, chloroform anhydrous, dichloroethane (DCE), trifluoromethanesulfonic acid (TFSA), dimethoxymethane (DMM), dichloroethane (DCE), and palladium(II) acetate. Phenantroline (phen), sulfuric acid (H_2SO_4, 98%), nitric acid (HNO_3, 70%), and potassium bromide (KBr) were used to synthesize the 4,5-diazafluoren-9-one monomer (DF) and iodomethane (CH_3I) and potassium carbonate (K_2CO_3) to N-methylisatin (MeIs). The model compounds were synthesized by combining IS, MeIS, and DF (or mixtures of two ketone monomers) with fluorobenzene (FB).

For the catalytic activity studies were employed different aryl halides (bromobenzene, 4-bromotoluene, 4-bromoanisole, 1-bromo-4-tert-butylbenzene, 1,3-dibromo-5-tert-butylbenzene, 1-bromonaphthalene, 4-bromobiphenyl, 9-Bromophenanthrene, bromopentamethylbenzene, 2-bromo-1,3,5-triisopropilbenzene, chlorobenzene, 4-chlorotoluene, 4-chloroanisole and 1-chloronaphthalene) and two boronic acids (phenylbonronic acid and 4-methoxyphenylboronic acid).

Other bases (such as sodium carbonate anhydrous, cesium carbonate, hydrogen sodium carbonate, and sodium hydroxide), and common solvents (such as distilled water, ethanol, methanol, acetone, dichloromethane (DCM), chloroform, tetrahydrofuran (THF), hydrochloric acid 35% (and dissolution of 4%) (HCl), anhydrous dimethylformamide (DMF) and toluene) were used in monomer synthetic process, catalytic reactions, and wash, extraction and neutralization processes. Magnesium sulfate anhydrous was used to remove water traces in the extraction processes.

All the reagents and solvents were purchased from different trading house (Fluorochem, Alfa Aesar, ABCR, Merck, Sigma-Aldrich, or Scharlab) with high-purity grade (> 97%) and were used without further purification.

Synthesis

1. Monomer synthesis

1.1. Synthesis of monomer 4,5-diazafluoren-9-one (DF)

DF was synthesized following the methodology described in the bibliography, and summarized in Figure M1.[183] In a first step, a mixture of H_2SO_4 (125 mL) and HNO_3 (63 mL) was carefully added into a flask placed in an ice bath containing a solid mixture of 1,10-phenantroline (12.4 g, 68.9 mmol) and KBr (12.8 g, 108 mmol). The reaction was left to reflux for 3 h, and then neutralized with an aqueous solution of NaOH, and extracted with chloroform. The organic layer was washed twice with distilled water, dried with magnesium sulfate anhydrous, and brought to dryness in a rotary evaporator. The product 1,10-phenantroline-5,6-dione (PHADO) was obtained with a 70% yield. Next, in a second step, PHADO (4.00 g, 19.0 mmol) was made to react with 0.25 M NaOH solution (200 mL) at 100 °C in a beaker until the volume was halved. Afterwards, the product was filtered, washed several times with distilled water, and dried at 50 °C under vacuum. Finally, the DF monomer was purified by filtration through aluminum oxide using chloroform as the eluent. An 81% yield (overall yield of 56%) was obtained. ^1H NMR spectrum of DF (500 MHz, $CDCl_3$); δ(ppm): 8.81 (dd, J = 5.0, 1.6 Hz, 2H), 8.00 (dd, J = 7.5, 1.6 Hz, 2H), 7.36 (dd, J = 7.5, 5.0 Hz, 2H). The spectrum is displayed in APPENDIX 1, Section 1.

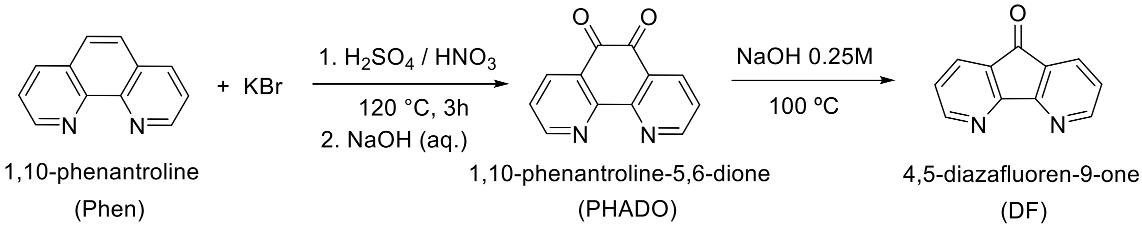


Figure M1. *Scheme of synthesis of DF*

1.2. Synthesis of monomer N-methylisatin (MeIS)

MeIS (1-Methylindoline-2,3-dione) was synthesized by employing the following methodology (summarized in Figure S2):[184,185] A 250 mL two-neck flask equipped with magnetic stirring and a nitrogen blanket was charged with IS (8.00 g, 54.4 mmol), K_2CO_3 (8.28 g, 59.8 mmol), CH_3I(3.38 mL, 54.4 mmol) and 110 mL of DMF. The reaction was stirred at room temperature for 12 h. Then, water was added to the mixture, and the product was extracted with DCM. After purifying by recrystallization in toluene, the dark orange solid was dried at room temperature under vacuum. The reaction yield was 97%. ^1H-NMR spectrum of MeIS (400 MHz, $CDCl_3$); δH (ppm):

7.65 – 7.56 (m, 2H), 7.13 (t, J = 7.5 Hz, 1H), 6.89 (d, J = 8.1 Hz, 1H), 3.25 (s, 3H). The spectrum is displayed in APPENDIX 1, Section 1.

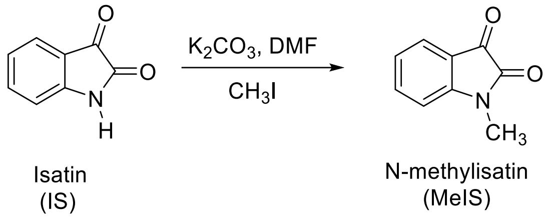


Figure M2. *Synthesis of MeIs*

2. Polymer synthesis

2.1. Polymer synthesis by polyhydroxyalkylation

Reaction conditions of polymers were optimized to obtain linear polymers (LPs) with high-molecular weight and porous organic polymer networks (POPs) with high surface areas, and high thermal and chemical stabilities. The superacid catalyzed polyhydroxylakylation reactions, which are used for the synthesis of both LPs and POPs, are dependent of multiple parameters such as the monomers' reactivity, the stoichiometry of monomers, the acidity of the medium, and the time and temperature. Thus, all of these parameters must be considered in the reaction optimizing process. Besides, the use of anhydrous solvents, high-purity monomers, and working in an inert atmosphere is crucial in these reactions.

The methodology of these reactions is based on studies about the protonation of aldehydes and ketones in highly acidic conditions.[152] In this work aromatic nucleophilic monomers, BP (difunctional one) and 135TPB and TRP (trifunctional ones), were combined with one or a mixture of two electrophilic monomers, IS, MeIS and DF (difunctional monomers), to obtain LPs and POPs, respectively, as shown in Figure M3. The acronyms of materials used in this PhD thesis are given in Table M1.

Table M1. *Acronyms of linear polymer synthesized by polyhydroxyalkylation reactions*

(a)

Acronym	Composition
LP-1	BP-IS (1:1)
LP-2	BP-MeIS (1:1)
LP-3	BP-DF (1:1)
LP-4	BP-DF-IS (2:1:1)
LP-5	BP-DF-MeIS (2:1:1)

(b)

Acronym	Composition
POP-1	TRP-IS (2:3)
POP-2	TRP-MeIS (2:3)
POP-3	135TPB-IS (2:3)
POP-4	135TPB-MeIS (2:3)
POP-5	135TPB-DF (2:3)
POP-6	135TPB-DF-IS (4:3:3)
POP-7	135TPB-DF-IS (8:3:9)

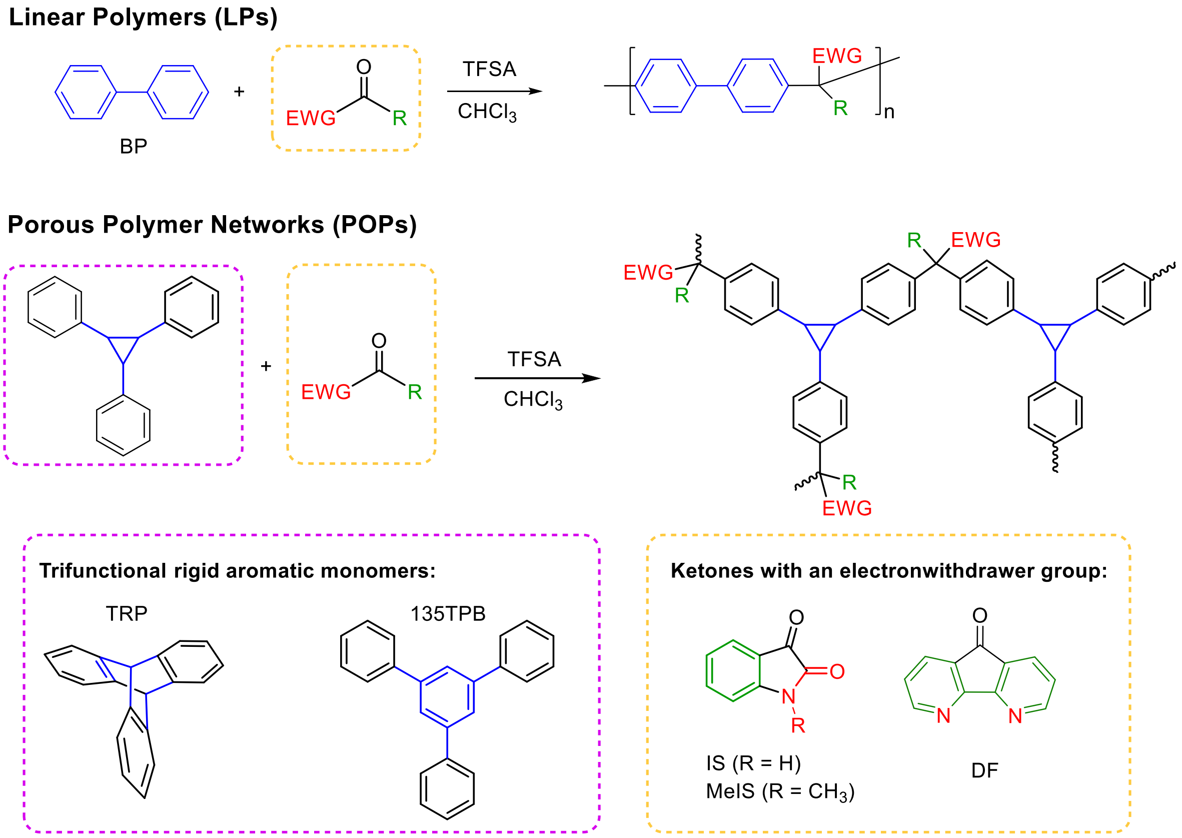


Figure M3. *General scheme of synthesis by SEAr of polymer materials.*

To optimize the synthesis of LPs and POPs two test types were accomplished. With the first one (Test 1), the easy formation of the di-coupled compound was studied. The reaction consists of the formation of mono-coupled monomer (entity 1) from which the di-coupled monomer (entity 2) is formed (Figure M4). FB was chosen because the reactions with this nucleophile are easy to follow by nuclear magnetic resonance of proton (^{1}H-NMR), carbon (^{13}C-NMR), and fluorine (^{19}F-NMR). For that study, the electrophile (IS, MeIS or DF) was made to react with a FB deficit in an acidic medium (TFSA/chloroform/electrophile/nucleophile mixture in molar ratio: 10/5/1/1 relative to the electrophile) at 35 °C for 24 h. The content of entities 1 and 2 in the reaction product was obtained from product mixtures from the ^{1}H- and ^{19}F- NMR spectra of the reaction. The spectra are displayed in APPENDIX 1, Section 2.

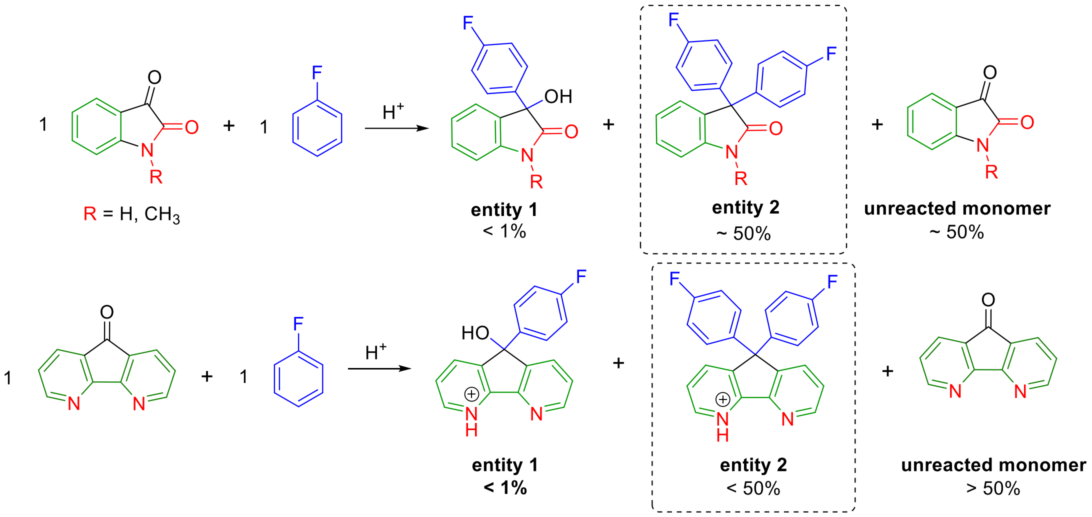


***Figure M4**. Test 1: Reactivity scheme of ketone monomers.*

In the second test (Test 2), the reactivity of the electrophiles was studied. For that purpose, similar reactions were made but using a stoichiometric nucleophile/electrophile molar ratio (TFSA/chloroform/electrophile/nucleophile: 10/5/1/2 relative to the electrophile). The ^{1}H-NMR spectrum of the reaction product from FB/DF (Figure M5) is shown as an example of the analysis carried out. The presence of DF monomer indicates that the reaction was not quantitative after 24 h. In contrast, the reaction with the mixture of IS and MeIS monomers was quantitative. All the spectra can be found in Appendix 1, Section 2.

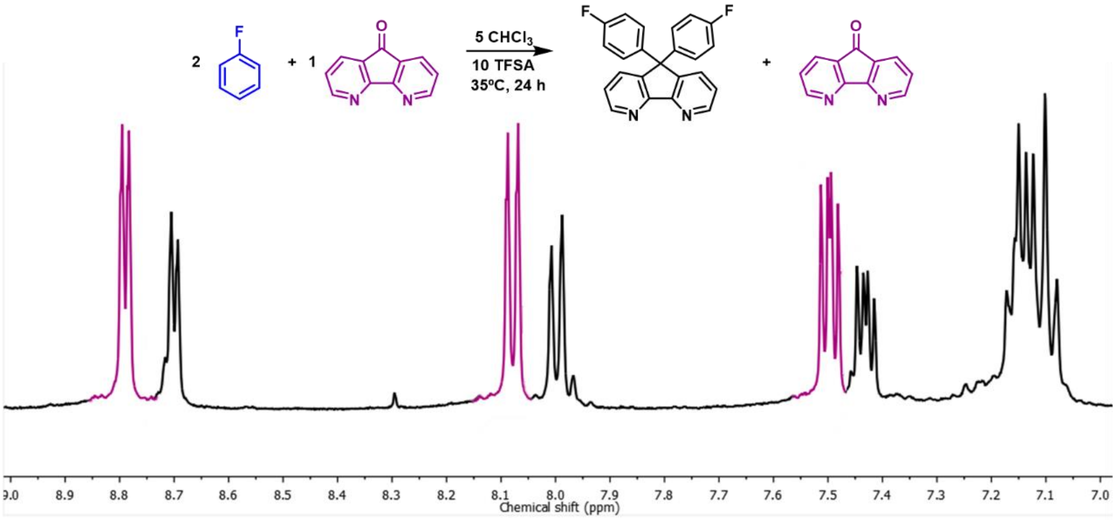


***Figure M5**. ^{1}H NMR spectrum of DF/FB reaction. Purple peaks correspond to protons of unreacted DF monomer and black ones to those of di-coupled compound.*

Competitive reactions between electrophiles were carried out in Test 2 using binary mixtures (1/1), in particular IS/MeIS and DF/IS ones. From IS/MeIS mixture, the ^{1}H-NMR spectrum of the reaction product showed the formation of the two di-coupled compounds in almost the same molar ratio (Figure M6). On the other hand, the competitive reaction using the DF/IS mixture revealed that DF reactivity was very much lower than that of IS or MeIS. The ^{1}H-NMR spectrum of the reaction product showed the formation of only the di-coupled compound derived from IS (Figure M7).

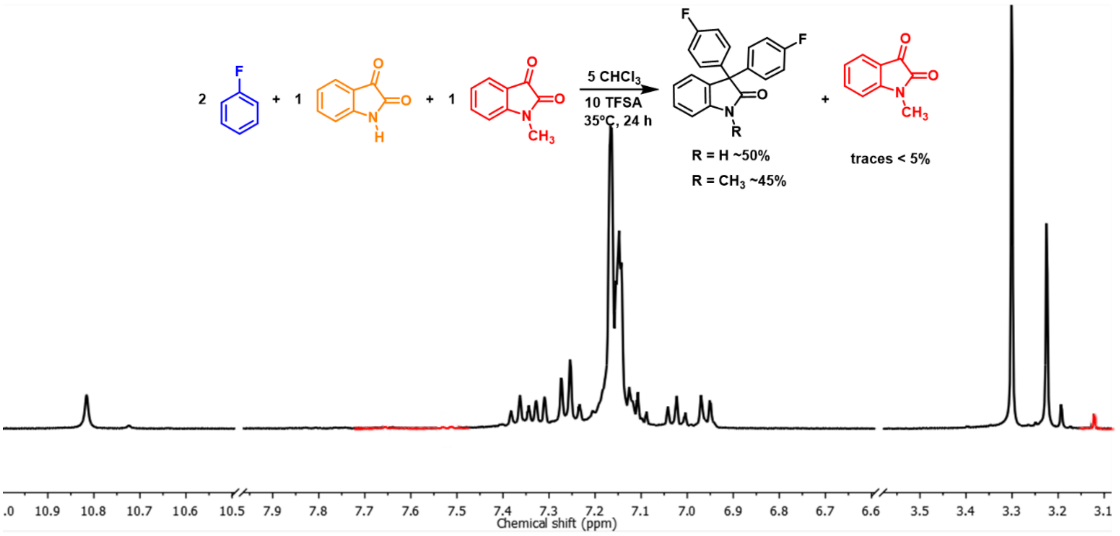


Figure M6. *^{1}H spectrum of product from IS/MeIS/FB competitive reaction. Black peaks correspond to protons of the two di-coupled compounds and very red small peaks to traces of MeIS monomer.*

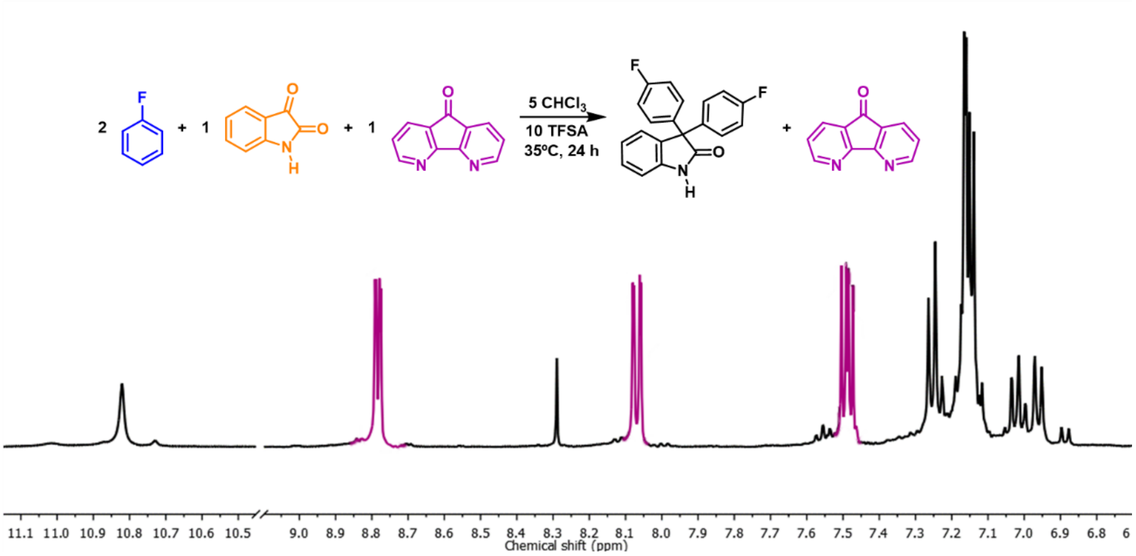


Figure M7*. ^{1}H NMR spectrum of the product from IS/DF/FB competitive reaction. Black peaks correspond to protons of IS/FB di-coupled compound and purple peaks to the unreacted DF monomer.*

2.1.1. Synthesis of linear polymers by S_EAr

Synthesis of BP-IS and BP-MeIS.

The procedure was as follows: dried monomers (8.2 mmol of BP and 8.2 mmol of IS (or MeIS) and 6 mL of chloroform anhydrous were added to a 50 mL three-neck flask equipped with mechanical stirring and nitrogen inlet and outlet. After the monomers became fully dissolved, the reaction flask was immersed into an ice-water-salt bath at – 5 °C, and then 12.4 mL of TFSA was added dropwise using an addition funnel for 20 min. The reaction was maintained at that temperature for an additional 30 min and at room temperature for 10 h. Then, the solutions were poured into a water/methanol (2:1) mixture. The polymers were filtered and then washed sequentially with a sodium bicarbonate aqueous solution, water, hot water, methanol/water mixture, and, finally, methanol. The polymers were dried at 120 °C and vacuum. The reaction yields were > 95%.

Synthesis of BP-DF, BP-IS-DF and BP-MeIS-DF.

It has been shown that the addition of an excess of the electrophile relative to nucleophile accelerates the polymerization reaction reducing the reaction time, which can last up to days when equimolecular amounts of nucleophile and electrophile are used. Thus, due to the lowest reactivity of DF, the synthesis of DF-containing polymers was carried out using 5% excess of DF relative to BP at 5 °C but maintaining the same acid molar ratio. The use of a lower temperature allows to decrease the kinetic reactivity of IS or MeIS when IS/DF or MeIS/DF mixtures are used to obtain the copolymers. Under these conditions, a high-viscosity solution was achieved in a short reaction time (a few hours), but a certain degree of cross-linking was always produced, obtaining insoluble polymers. Therefore, finally, it was considered convenient to use a stoichiometric ratio of monomers and to maintain the reaction temperature at 5 °C for a long time.

The optimized synthesis of copolymers was as follows: 8.2 mmol of BP, 4.1 mmol of DF, 4.1 mmol of IS (or MeIS) and 6 mL of chloroform anhydrous were charged into a 50 mL three-neck flask, equipped with mechanical stirring, under nitrogen atmosphere. The procedure was similar to that described above, but the reaction was maintained at – 5 °C for 20 min after adding the TFSA (12.4 mL) and then at 5 °C for 11 days. The work-up and washed process was the same as the one described previously. The reaction yields of all of the LPs were > 95%.

2.1.2. Synthesis of Porous Organic Polymers by S_EAr

The first family of porous polymer networks for this PhD thesis were synthesized by reacting the difunctional nucleophilic monomers used in the LPs (or mixtures of IS and DF), with trifunctional nucleophilic monomers (TRP and 135TPB).

The homo-POPs synthesized from IS or MeIS were prepared using TRP or 135TPB as trifunctional aromatic monomer in a 2/3 nucleophile/electrophile molar ratio following the methodology previously employed in our research group.[148] The procedure was as follows, a three neck Schleck mechanically stirred and provided with nitrogen inlet and outlet was charged with 13.8 mmol of TRP (or 135TPB) and 20.8 mmol of IS (or MeIS), which were dissolved in anhydrous chloroform (15 mL). Then, the mixture was cooled with a salt-ice-water bath and 30 mL of cold TFSA was slowly added (15–20 min). The mixture was kept at a low temperature and after 30 min more it was heated to room temperature. After 5 days stirring at room temperature, water was added into the flask to remove the acid excess and the solid was filtered and sequentially washed with water, methanol, warm acetone and warm chloroform. The product was obtained in a yield higher than 95% after drying at 150 °C under vacuum for 12 h.

The methodology described above could not be used to synthesize the polymers containing DF as the yield was not quantitative. After evaluating different conditions to synthesize these POPs, the procedure that is described below was chosen as the best one to prepare these materials. Under a nitrogen atmosphere, monomers and chloroform anhydrous were added to the flask and mechanically stirred. The mixture was cooled to about 0 °C and cold TFSA was added drop by drop. Afterward, the cold bath was kept for 30 min, then the mixture was heated to room temperature for 24 h and 60 °C for 96 h. Cold water was added into the flask to quench the reaction and remove the acid excess. The polymer was filtered and washed again with a sodium bicarbonate solution to deprotonate the pyridine groups. The POP was sequentially washed with water, methanol, acetone, and chloroform. Finally, the obtained brown powder was dried at 180 °C under vacuum and characterized. Spectra of all of these porous polymers are given in Appendix 2.

2.2. Synthesis of Porous Organic Polymers via a knitting methodology

The second family of POPs was based on phosphine polymers (PP) synthesized by using a *knitting* methodology, resulting in hyper-cross-linked polymers (POPs-HCP). Three aromatic diphosphines (DPPE, DPPP or DPPB), which differ in the length of the aliphatic chain that bind the two phosphorous atoms (2, 3 or 4 methylene groups, respectively). The knitting methodology consisted of a Friedel-Craft reaction, in which trifunctional aromatic monomers, 135TPB (or TPP), and one of the aromatic diphosphines (tetrafunctional monomer) connected the aromatic rings through methylene groups using DMM as cross-linker (Figure M8). In addition, other similar polymers were synthesized by incorporating an additional bifunctional nucleophilic monomer, BP, to obtain materials with controlled meso-and micro-porosity.

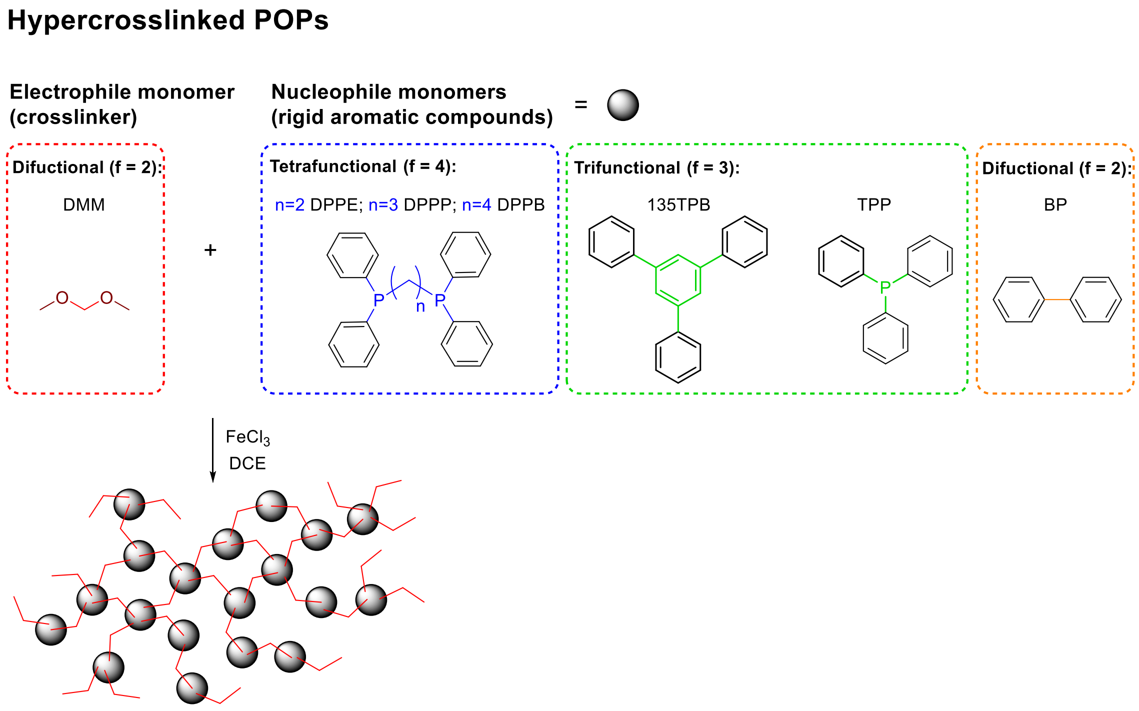


Figure M8. *General scheme of synthesis by knitting of polymer materials*

The optimization of the reaction was focused on obtaining cross-linked polymers with high surface areas. Several parameters were studied during the optimization process: excess of $FeCl_3$, DMM, and DCE, temperature, reaction time, and washing protocol. The conditions selected to prepare these POPs used a mixture of electrophile/nucleophile/$FeCl_3$ in a ratio 4/1/1 attending to the functionality (cf. Figure 8, f = 2, 3 or 4) of each monomer. A general procedure of the synthesis is described below: 135TPB (4 eq, f = 3), BP (12 eq or 0 eq, f = 2) and 3 eq of diphosphine (3 eq, f = 4) (or TPP (4 eq, f = 3) were added to a flask equipped with mechanical stirring and nitrogen atmosphere, then $FeCl_3$ (96 eq or 48 eq when POP-HCP is synthesized without BP) were added. Subsequently, the mixture was cooled with an ice bath, and 80 – 100 mL of DCE and

DMM (96 eq or 48 eq when POP-HCP is synthesized without BP, f =2) were added. The mixture was mechanically stirred for 30 min and then sequentially was heated to room temperature for 30 min, to 45 °C for 24 h and to 80 °C for 72 h. The reaction was quenched by adding methanol into the reaction flask, then, the solid was filtered and sequentially washed with hot methanol, HCl 4% and THF. The acronyms and the molar ratio of the nucleophiles mixture used in each POP are displayed in Table 2.

Table M2. *Acronyms of POPs synthesized by knitting*

Acronym	Composition
PP-1	135TPB-TPP (1:1) - DMM
PP-2	135TPB-BP-TPP (1:1:3) - DMM
PP-3	135TPB-DPPE (4:3) - DMM
PP-4	135TPB-BP-DPPP (4:3:12) - DMM
PP-5	135TPB-DPPP (4:3) - DMM
PP-6	135TPB-BP-DPPE (4:3:12) - DMM
PP-7	135TPB-DPPB (4:3) - DMM
PP-8	135TPB-BP-DPPB (4:3:12) - DMM

3. Synthesis of confined catalysts

The heterogeneous catalysts were prepared by immersion of POPs in a palladium acetate solution in DCM. For POPs-S_EAr containing DF, the amount of palladium acetate was added stoichiometrically to the number of DF moieties. For POPs-HCPs containing diphosphines, palladium acetate was added in a molar ratio of 0.5 palladium salt/phosphorous atom. In all the cases, the POP was dispersed in dichloromethane with Ultra-Turrax at 12000 rpm and after adding palladium acetate, the mixture was stirred under a nitrogen atmosphere at room temperature in the dark for 72 h. Then, the catalyst was filtered and sequentially washed using DCM and acetone. The heterogeneous catalysts were dried at 60 °C under vacuum.

4. Membrane preparation

4.1. Pristine polymer membranes

Pristine polymer membranes were prepared by casting method. First, solubility tests of LPs obtained were carried out to choose the organic solvent. Then, amounts between 100 and 50 mg of LPs were weighted to be dissolved in 25 mL of the adequate solvent (concentration 10% - 5% (w/v)). The polymer solution was filtered through a Symta® glass-fiber syringe filter with a pore size of 3.1 µm, and it was then poured into a glass ring placed on a leveled glass plate. Subsequently, the polymer solutions were heated to a particular temperature, depending on the solvent’s boiling temperature, using a digital hot plate/magnetic stirrer (Figure M9). Thus, polymer solutions in low-boiling solvents (e.g. $CHCl_3$ and THF) were heated to 30 °C and those in high-boiling solvents (e.g. DMF, DMAc, and NMP) to 60 °C to remove most of the solvent. Afterward, the membranes were peeled off from the glass and subjected to the following thermal treatment under vacuum: 80 °C/30 min, 100 °C /1 h, 120 °C /30 min, 150 °C /1 h, and 180 °C/12 h. Homogeneous membranes with thickness values between 40 and 60 µm were obtained.

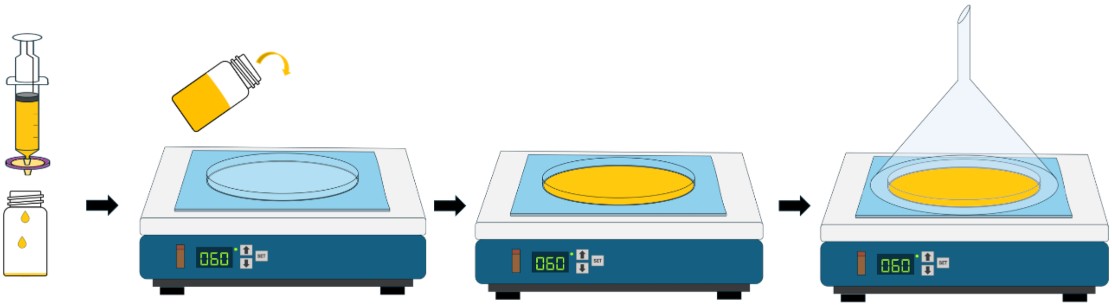


Figure M9. *Preparation of pristine polymer membranes by casting method.*

4.2. Mixed Matrix Membranes

The casting methodology to prepare Mixed Matrix Membranes (MMMs) was more complex, because a suspension of the selected POP-S_EAr as filler must be prepared apart from the polymer solution. The matrix polymer (600 mg) was dissolved in 4 mL of a particular solvent and the POP (100 mg) was stirred in 4 mL of the same solvent. The POP suspension was sonicated to adequately disperse the polymer network particles, preventing the temperature from rising by using a water bath. Then, a priming technique was used to facilitate the interaction between matrix and filler by adding a third part of the filtered polymer solution to the POP suspension.[158] The mixture was sonicated for 2 min, the rest of the matrix solution was then added and the final suspension was magnetically stirred for 10 min. From here, the procedure was the same as the one described above; briefly, the final suspension was poured on the glass, heating to a particular temperature to remove most of the solvent, the mixed matrix membrane was then peeled off from the glass and subjected to the same thermal treatment. The complete procedure is schematized in Figure M10.

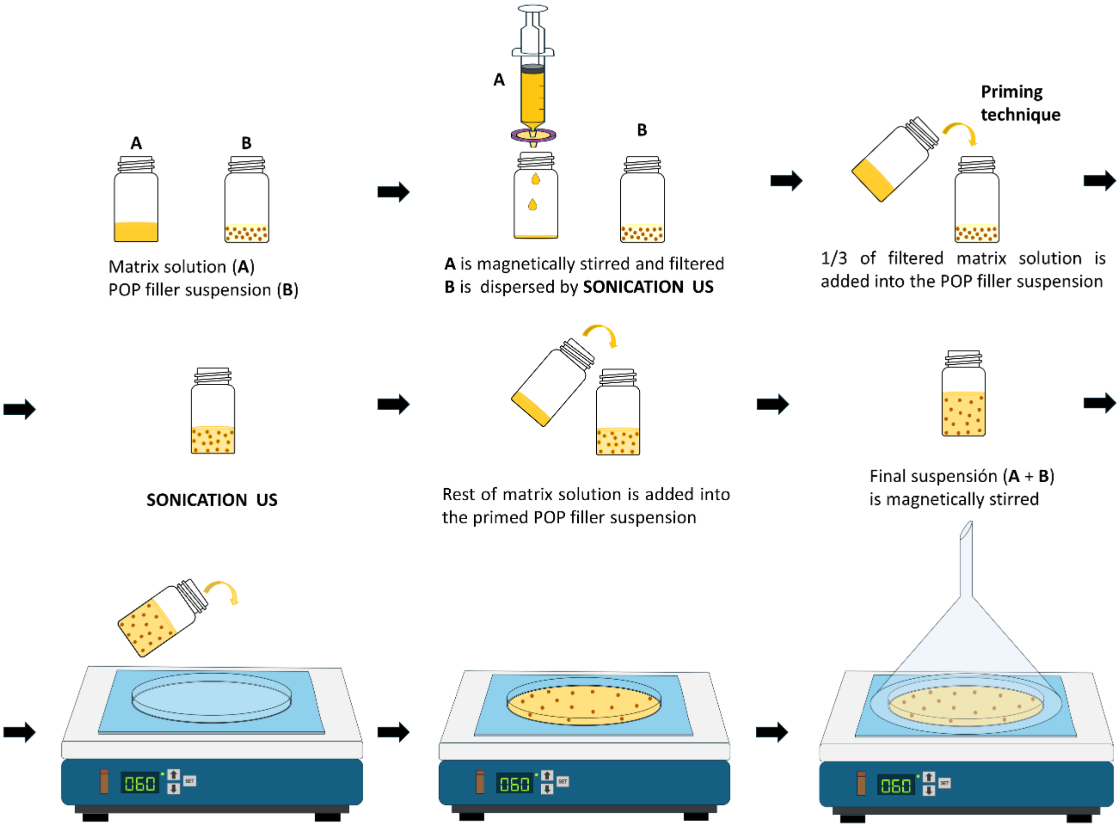


Figure M10. *Preparation of mixed matrix membranes by casting method.*

Study of Catalytic Activity

The catalytic activity of the heterogeneous catalysts was evaluated in Suzuki-Miyaura cross-coupling reactions. First of all, the best conditions of solvent and base were tested with the DF catalysts, being chosen a mixture of water/ethanol as solvent and Na_2CO_3 as a base. These were chosen based on the results observed in an optimization process and prioritizing the use of environmentally friendly and inexpensive conditions. Leaching tests were performed to ensure that the metal was correctly anchored within the materials. Once the correct anchoring of the metal to the POPs was confirmed, its catalytic activity was evaluated, using different aryl halides, changing parameters such as time, temperature, and catalytic amount. In addition, the recyclability of the catalytic heterogeneous materials was studied for both types of polymers.

Gas Transport Properties

Permeability (P) is defined as the amount of permeating gas (A) across the membrane per unit time and unit area (J_A) scaled on the pressure drop and the membrane thickness (l):

$$P = \frac{J_A{}^{l}}{p_{A,0} - p_{A,l}}$$

where $p_{A,0}$ and $p_{A,l}$ are the partial pressures of the gas A on the upstream and downstream sides, respectively.

In the framework of the solution-diffusion model and Fick's law, when the downstream pressure is significantly lower than the upstream pressure, the permeability of gases A and B in a specific polymer membrane is influenced by the product of their solubility (S) and diffusion coefficient (D).

$$P = D \cdot S$$

Consequently, gas A being significantly more permeable than gas B can be attributed to one of the following reasons:

gas A has a higher diffusion rate

gas B has greater solubility in the membrane (indicating stronger gas/polymer interaction)

a combination of both factors

Generally, gas separation in polymer membranes relies on variations in either gas diffusivity (diffusivity-selective or size-sieving materials) or gas solubility (solubility-selective materials).

The permeability values of the neat membranes and MMMs in this PhD thesis were evaluated by measuring pure gases (He, O_2, N_2, CH_4, and CO_2) at 35 °C using a constant volume/variable pressure apparatus. Once the membrane was placed in the cell, the whole system was degassed for about 12 h under high-vacuum to remove any trace of humidity. Then, a feed pressure of 3 bar was applied to the membrane and the increase in permeate pressure was recorded as a function of time until the steady state was achieved. Gas permeability was obtained from the following equation:

$$P = \frac{273.15}{76} \cdot \frac{V \cdot l}{\pi \cdot r^2 \cdot T \cdot p_0} \cdot \frac{dp}{dt} \cdot 10^{10}$$

where V is the volume in cm^3 in the permeate compartment, l is the membrane thickness in cm, πr^2 is the membrane area in cm^2, T is the temperature in K, p_0 is the feed pressure in bar and dp/dt is the rate of pressure change in the downstream volume in units of mbar s^{-1}. P is expressed in barrer [1 barrer = 10^{-10} (cm^3(STP) cm cm^{-2} s^{-1} $cmHg^{-1}$)]. Scalar factors are included to reference the molar flux at standard pressure and temperature (76 cmHg and 273.15 K).

The ideal gas **selectivity** (or gas permselectivity) **($\alpha_{A/B}$)** is the ability of a membrane to separate a pair of gases A and B and is calculated from the gas permeability ratio:

$$\propto_{A/B} = \frac{P_A}{P_B}$$

An ideal membrane for gas separation must simultaneously exhibit high permeability (membrane productivity) and high selectivity (the ability to discriminate between specific components in a mixture). Additionally, it should possess high chemical and thermal stability, excellent mechanical resistance under operating conditions, a long operational lifespan, and be cost-effective and free of defects in production.

The trade-off in separation membranes between permeability and selectivity in which the more permeable materials tend to be the less selective and *vice versa* was first highlighted by Robeson in 1991.[186] Since then, the performance benchmark for a given gas pair has been represented by an "upper bound" line fitted to the best-performing materials on a double-logarithmic plot of selectivity versus permeability for the faster gas, known as Robeson plots. This means that no data points exist above these empirically determined upper bounds. The position of a membrane's gas permeability data relative to these upper bounds on a Robeson plot indicates its potential for gas separation applications. However, the ongoing development of membrane materials with improved performance continually shifts these upper bounds, as illustrated in Figure 11. As a result, Robeson updated the database in 2008,[187] Pinnau *et al.* did so in 2015,[188] and McKeown *et al.* proposed new upper bounds for several important gas pairs in 2019,[189] based on the permeability data of a series of ultrapermeable polymers they synthesized.

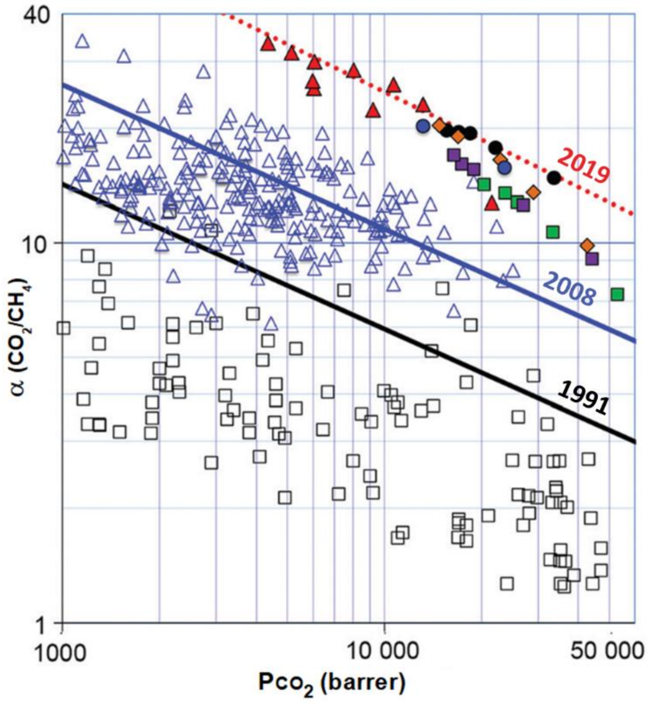


Figure M11. *Robeson plot for* CO_2/CH_4 *separation.*[189]

Techniques

- **Fourier-transform infrared-attenuated total reflectance (FTIR-ATR) spectra** was registered in a Perkin Elmer Spectrum RX-I FT-IR spectrometer equipped with an ATR accessory Pike GladiATR-210 at IU CINQUIMA/University of Valladolid (UVa) to identify characteristic bands and functional groups of all of the synthesized compounds (monomers and polymers) and membranes.
- **^{1}H-NMR and ^{13}C-NMR** spectra were recorded on an Agilent MR-500MHz or a Bruker Avance 400 MHz spectrometer at the Laboratory of Instrumentals Techniques (LTI)/IU CINQUIMA/UVa, to confirm the chemical structure of monomers and LPs. DMSO-d_6 and $CDCl_3$ solvents or a mixture $CDCl_3$/TFA-d were used. **^{1}H-and ^{9}F-NMR** were used for the reactivity study of IS, MeIS, and DF monomers.
- **Solid state ^{13}C and ^{31}P cross-polarization magic angle spinning NMR spectra (CP-MAS ^{13}C and ^{31}P NMR)** spectra were registered in a Bruker AVANCE TM 400WB spectrometer at the Institute of Science and Technology of Polymers ICTP/CSIC to obtain information about the chemical structure of POPs-S_EAr and POPs-HCPs.
- **Thermogravimetric analysis (TGA)** was carried out using a TA-Q500 instrument operating under a continuous nitrogen or air flow (60 mL/min) at ICTP/CSIC and in a temperature range between 30 and 850 °C. A Hi-Res method at a heating rate of 20 °C min^{-1} and sensibility and resolution parameters of 1 and 4, respectively, was carried out to determine the thermal stability of the polymers in a nitrogen atmosphere. This method also was used to know the temperature range to which takes place the reduction Pd(II) to Pd(0) in the confined catalysts. Besides, dynamic TGA scans at 10 °C/min in an air atmosphere were made to calculate the metal content from the residue at 850 °C.
- **Differential scanning calorimetric (DSC)** measurements were run at 20 °C/min and nitrogen atmosphere (50 mL/min) using a DSC Q-2000 Analyzer of TA Instruments at IU CINQUIMA/UVa. For measurements, hermetic aluminum pans were used with approximately 6 mg of sample. Thermograms were collected from 50 °C to 375 °C. From these measurements, the glass transition temperature of LCPs, neat membranes and MMMs were determined from the second heating run.
- **Scanning Electron Microscopy (SEM)** images were taken with a QUANTA 200 FEG FESEM at the LTI/UVa. The high-resolution images allow us to study the morphology of all porous organic polymers and membranes. In the case of the porous organic polymers, a small power

quantity was deposited on carbon tape. For the MMMs, the images correspond to the cryogenic cross-section fracture of the samples to study the dispersion and size of the filler particles in the polymer matrix.

- **Inherent viscosities** of polymers were measured in a Lauda iVisc using a standard Ubbelohde viscometer placed into a water bath at 30 °C in ICTP/CSIC. Polymer solutions were prepared by dissolving 125 mg of LP in 25 mL of particular solvent, and they were filtered using Symta® glass-fiber syringe filter with a pore size of 3.1 µm before adding them to the Ubbelohde viscosimeter. For a family of polymers, their inherent viscosities can be related to molecular weight if they are measured in the same solvent; i.e., the higher intrinsic viscosity the higher molecular weight.
- **Bulk density** of membranes was measure in SMAP/UVa using a top-loading electronic XS105 Dual Range Mettler Toledo balance which is coupled with a density kit operating on Archimedes' principle. Fractional Free Volume (FFV) was estimated applying the semiempirical method Austin Model 1 (AM1) by using the Hyperchem Molecular Modeling Program. These measured were carried out as is describe in bibliography.[158]
- **Wide-Angle X-ray Scattering (WAXS)** patterns were recorded on a Bruker D8 ADVANCE diffractometer provided with a Goebel Mirror and Vantec detector using CuK_α (wavelength λ= 1.54 Å) radiation at LTI/UVa to obtain information about amorphous nature of LPs and POPs and about the chain packing density in the pristine membranes and MMMs. The most probable intersegmental distances (d) in the chain packing were estimated from the well-known Bragg's Law (λ=2dsenθ, being θ the diffraction angle corresponding to the maxima in the amorphous halo).
- **SEM-energy-dispersive X-ray spectroscopy (SEM-EDX)** was carried out with a scanning electron microscope ESEM (QUANTA 200 FEG) ESEM at LTI/UVa. A qualitative analysis of the material chemical composition can be determined by this technique, in this research work was studied the palladium distribution in the confined catalysts.[190–193]
- **X-ray photoelectron spectroscopy (XPS)** measurements were registered in a SPECS device using a PHOIBOS 100 hemispherical electron energy analyzer and a five-channel multi-Channeltron detector at the Institute of Carbon Science and Technology INCAR/CSIC. XPS is a powerful tool to identify the oxidation states of elements. Here, XPS was used to study the coordination states of palladium species inside the POP catalysts before and after use. Deconvolution of the Pd(0) and Pd(II) contributions to the XPS spectra was made with the Origin 9.5 program.[194]

- **Inductively coupled plasma optical emission spectroscopy** (**ICP-OES)** was carried out by employing a Varian 725-ES device at LTI/UVa to determine the palladium content in the POPs catalysts.

- **Gas chromatography-mass spectrometry (GC-MS)** was registered using an Agilent Technologies 6890N gas chromatograph coupled to an Agilent Technologies 5973 inert mass spectrometer at LTI/UVa to determine the yield and conversion of catalytic tests.

- **Helium pycnometry** was employed to determine the skeletal density of the POPs-S_EAr by using an AccuPyc 1340 apparatus at ICTP/CSIC.

- **Low-pressure nitrogen adsorption/desorption isotherms at –196 °C (77 K).** The isotherms of all of the POPs were measured using a 3Flex Micrometrics volumetric analyzer at the University of Orleans (Chapter II) and an ASAP 2020 Micromeritics device at the Institute of Materials Science (ICMM/CSIC) (Chapter I and III) to evaluate their textural properties. Prior to perform the measurements, the samples were degassed under a high vacuum to eliminate humidity traces and any other adsorbed gases. Thus, the IS- and MeIs-based POPs were degassed at 125 °C for 18 h, DF-based POPs at 250 °C for 10 h, and diphosphine-based POPs at 180°C for 16 h. The following parameters were determined from the low-pressure isotherms: the specific surface area (S_{BET}) calculated by the well-known Brunauer−Emmett−Teller equation, the total pore volume (V_{total}) defined as the volume of adsorbed nitrogen at 0.98 relative pressure, the micropore volume (V_{micro}) calculated from the Dubinin−Radushkevich (DR) equation. The pore size average and distribution (PSD) was estimated by applying the Barret-Joyner-Halenda (BJH) method in Chapters I and III and the 2D-NLDFT-HS model in Chapter II.[195–197]

Chapter I. Polymer Materials Derived from the S_EAr Reaction for Gas Separation Applications

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Abstract

A set of linear polymers were synthesized utilizing an electrophilic aromatic substitution reaction (S_EAr) between biphenyl and ketone/s containing electron-withdrawing groups (isatin, IS; N-methylisatin, MeIS, and 4,5-diazafluoren-9-one, DF). Optimization of the polycondensation reaction was made to obtain high molecular weight products when DF was used as monomer, which has not previously been used for linear polymer synthesis. Due to the absence of chemically labile units, these polymers exhibited excellent chemical and thermal stability. Linear S_EAr polymers were blended with porous polymer networks derived from IS and MeIS, and both neat/mixed materials were tested as membranes for gas separation. The gas separation properties of both, pristine polymers and mixed matrix membranes, were good, showing some polymer membrane CO_2 permeability values higher than 200 barrer.

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Chapter II. Porous Organic Polymers Containing Active Metal Centers for Suzuki−Miyaura Heterocoupling Reactions

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Abstract

A new generation of confined palladium(II) catalysts covalently attached inside of porous organic polymers (POPs) has been attained. The synthetic approach employed was straightforward, and no prerequisite of making any modification of the precursor polymer was needed. First off, POP-based catalytic supports were obtained by reacting one symmetric trifunctional aromatic monomer (1,3,5-triphenylbenzene) with two ketones having electron-withdrawing groups (4,5-diazafluoren-9-one, DF, and isatin) in superacidic media. The homopolymers and copolymers were made using stoichiometric ratios between the functional groups and they were obtained with quantitative yields after an optimization of reaction conditions. Moreover, the number of chelating groups (bipyridine moieties) available to bind Pd(II) ions in the catalyst supports was modified using different DF/IS ratios. The resulting amorphous polymers and copolymers showed high thermal stability, above 500 °C, and moderate-high specific surface areas (from 760 to 935 m^2/g), with high microporosity contribution (from 64% to 77%). Next, POP-supported Pd(II) catalyst were obtained by simple immersion of the catalyst supports in a palladium(II) acetate solution, observing that the metal content was similar to that theoretically expected according to the amount of the bipyridine groups. The catalytic activity of these heterogeneous catalysts was explored for the synthesis of biphenyl and terphenyl compounds, via the Suzuki-Miyaura cross-coupling reaction using a green solvent (ethanol/water), low palladium loads and aerobic conditions. The findings showed excellent catalytic activity with quantitative product yields. Additionally, the recyclability of the catalysts, by simply washing it with ethanol, was excellent, with a sp^2–sp^2 coupling yield higher than 95% after 5 cycles of use. Finally, the feasibility of these catalysts to be employed in tangible organic reactions was assessed. Thus, the synthesis of a bulky compound, 4-4'-dimethoxy-5'-

tert-butyl-m-terphenylene, which is a precursor of a thermally rearrangement monomer, was scaled-up to 2 g, with high conversion and 96% yield of pure product.

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Chapter III. Palladium Catalysts Supported in Microporous Phosphine Polymer Networks

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Abstract

A new family of microporous organic polymers (POPs) containing diphosphine-derivates synthesized by knitting via Friedel-Crafts were attained using different diphosphines, 1,3,5-triphenylbenzene and biphenyl as nucleophile aromatic groups, dimethoxymethane as electrophile linker, and $FeCl_3$ as promotor catalyst. These new amorphous and tridimensional polymer networks showed moderate thermal stability, high surfaces areas (between 765 and 1305 m^2/g) and high microporosity. Furthermore, these new materials could be coordinated to palladium acetate, being the diphosphine-derivate the anchor center, and could be used as heterogeneous catalysts in Suzuki-Miyaura reactions. Using small charges of catalysts and green conditions, the supported catalysts exhibited excellent catalytic activity and good recyclability, without significant loss of activity or Pd leaching after five consecutive reaction cycles.

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Main conclusions

In this Ph.D. memory, new polymer materials having chelating groups able to interact with metals (bipyridine derived from 4,5-diazafluoren-9-one (DF) or phosphorus atoms coming from 1,2-bis(diphenylphosphino)ethane (DPPE), 1,3-bis(diphenylphosphino)propane (DPPP) and 1,4-bis(diphenylphosphino)butane (DPPB)) were obtained using two different electrophilic aromatic substitutions (S_EAr) synthetic methodologies.

Although it was determined in this research work that the bipyridine monomer DF possesses lower reactivity than other comonomers widely employed in S_EAr reactions, such as isatin (IS) and N-methylisatin (MeIS), it could be used in the synthesis of polymers (linear and networks) after optimization of the reaction conditions. Thus, two families of polymeric materials with excellent properties were obtained fromDF. The first family gave rise to high molecular weight linear polymers (LPs), which showed good mechanical properties when processed as membranes. The second family consisted of amorphous microporous polymer networks (POPs) with high surface areas (760-935 m^2/g). Both polymeric materials showed excellent chemical and thermal stabilities, above 450 °C. The DF-derived linear polymers, alone or combined with some POPs developed in this report (forming mixed matrix membranes, MMMs), could be tested in gas separation applications, presenting good values.

Also, a POP family was obtained from aromatic diphosphines; DPPE, DPPP, and DPPB, by direct alkylation, using the as-named *knitting* methodology, using dimethoxymethane as a cross-linker. These amorphous hypercrosslinked microporosity polymers displayed moderate thermal stabilities and high surface areas (760-1300 m^2/g).

Heterogeneous Pd(II) catalysts were obtained by reacting POP precursors with palladium(II) acetate. These metal-containing POP materials were studied as catalysts in Suzuki-Miyaura cross-coupling reactions, showing excellent catalytic activity, using a green solvent (ethanol/water), which was maintained for several runs without significant Pd(II) leaching. The heterogeneous Pd(II) catalysts gave excellent catalytic efficiency when the reactions were scaled up, suggesting that these materials could be valid for industrial applications.

Therefore, attending to these results, the great versatility of the new materials designed and obtained in this PhD thesis was confirmed, since they were able to be efficiently employed in different applications such as gas separation or heterogeneous catalysis.

Conclusiones

En esta memoria de tesis doctoral, se han obtenido nuevos materiales poliméricos utilizando dos metodologías sintéticas diferentes de sustitución aromática electrofílica (S_EAr) con grupos bidentados capaces de interaccionar con metales. Concretamente, los grupos bidentados quelato empleados han sido la bipiridina derivada de 4,5-diazafluoren-9-ona (DF) y átomos de fósforo procedentes de 1,2-bis(difenilfosfino)etano (DPPE), 1,3-bis(difenilfosfino)propano (DPPP) y 1,4-bis(difenilfosfino)butano (DPPB)).

En este trabajo de investigación se determinó que el monómero de bipiridina DF posee menor reactividad que otros comonómeros ampliamente empleados en reacciones S_EAr, como la isatina (IS) y la N-metilisatina (MeIS), sin embargo, se demostró que dicho monómero, tras optimizarse las condiciones de reacción, puede utilizarse en la síntesis de polímeros (lineales y redes). Por ello, a partir de DF se obtuvieron dos familias de materiales poliméricos con excelentes propiedades. La primera familia dio lugar a polímeros lineales (LPs) de alto peso molecular, que mostraron buenas propiedades mecánicas cuando se procesaron como membranas. La segunda familia dio lugar a redes poliméricas amorfas microporosas (POP) con áreas superficiales elevadas (760 – 935 m^2/g). Ambos materiales poliméricos, LPs y POPs, mostraron una excelente estabilidad química y térmica, por encima de 450 °C y se emplearon en aplicaciones de separación de gases y catálisis, respectivamente.

Los LPs derivados de DF, solos o em forma de membranas de matriz mixta (MMMs) al ser combinados con algunos POPs desarrollados en esta memoria, pudieron ensayarse en aplicaciones de separación de gases, presentando buenos valores.

Además de estas dos familias, se obtuvieron distintas familias de POPs sintetizadas por alquilación directa a partir de difosfinas aromáticas (DPPE, DPPP y DPPB), utilizando la metodología comúnmente denominada *knitting*, empleando dimetoximetano como agente reticulante. Estos polímeros amorfos hiperreticulados de microporosidad mostraron estabilidades térmicas moderadas y áreas superficiales elevadas (760 –1300 m^2/g).

A partir de las distintas familias de POPs sintetizadas con monómeros con grupos quelantes se obtuvieron catalizadores heterogéneos de Pd(II). Para ello, los POPs se hicieron reaccionar con acetato de paladio(II). Estos POPs anclados a Pd(II) se estudiaron como catalizadores en reacciones de acoplamiento cruzado Suzuki-Miyaura utilizando un disolvente verde (etanol/agua), mostrando una excelente actividad catalítica, que se mantuvo durante varias ejecuciones sin *leaching*. Además, estos catalizadores mostraron excelente eficiencia catalítica cuando se escalaron las reacciones, lo que sugiere que estos materiales podrían ser válidos para aplicaciones industriales.

Por tanto, atendiendo a estos resultados, se confirmó la gran versatilidad de los nuevos materiales diseñados y obtenidos en esta tesis doctoral, ya que pudieron ser empleados eficientemente en diferentes aplicaciones como la separación de gases o la catálisis heterogénea.

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