Sorption of Gases and Liquids by Polymers of Intrinsic Microporosity (PIMs)

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(43 000 words)
Abstract

This study presents the synthesis of polymers of intrinsic microporosity and the investigation of their microporosity using gas sorption and adsorption of liquids and vapours.

Microporous polymeric materials PIM-1, TAPIM-1, PIM-2 and PIM-7 were synthesised using step-growth polymerisation. The microporosity of these materials was studied using gas sorption and adsorption of molecules in the liquid phase.

A procedure to validate gas sorption methods was undertaken before being used to characterise microporous materials. The sorption methodology was validated using standard reference materials (SRMs) and collaborative testing, and the PSD evaluation was validated using a well defined crystalline material.

Different approaches to obtaining pore size distribution (PSD) data were dealt with. Gas sorption methods that use CO$_2$ at 273 K and at 303 K, N$_2$ at 77 K, H$_2$ at 77 K, and Xe (298 K) to determine PSD were compared. The Horvath-Kawazoe (HK) model was presented as the preferred model and the N$_2$, CO$_2$ and H$_2$ sorption data were treated under this approach. CO$_2$ PSD data at 273 K and at 303 K was compared against N$_2$ PSD data and a novel complementary relationship established. PIM-1 samples in film form and powder form were used to investigate the effect of sample form on the sorption properties of the material. PIM-1, PIM-2, TAPIM-1, ethano-anthracene PIM-1 copolymers, and triptycene based PIMs were used to investigate the influence of polymer structure on gas sorption properties.

The free volume properties of a PIM-1 ethano-anthracene copolymer (PIM-CO1-40), was compared against PIM-1. A number of independent techniques, namely N$_2$ sorption, Xe sorption, Positron annihilation lifetime spectroscopy (PALS), and $^{129}$Xe NMR were used to probe the free volume. The time dependence of free volume and its bearing on diffusivity of PIM-1 membranes was investigated.

Water, chloroform and simple alcohols were used to investigate adsorption in the liquid and vapour phases. Interaction with PIM-1 the aromatic ether linkage and the nitrile group produced frequency shifts in ATR-FT-IR spectra. These frequency shifts were used to compare relative strengths of the hydrogen bonds.
DECLARATION

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PREFACE

The author graduated from the University of Zimbabwe with a BSc (Honours) Chemistry degree and, after a 2 year stint as a science teacher, proceeded to study for an MSc in Analytical Chemistry at the same university. Thereafter, he worked in research and for a sugar refinery before taking up a job as a university lecturer in Zimbabwe. After moving to England in 2002, he underwent the Graduate Teacher Programme (GTP) training at Ossett College in Wakefield and subsequently worked as a teacher at St. Bernard’s High School, Rotherham. He studied for an MA in Educational Studies at the University of Sheffield. He then worked as a Chemist with a polymer manufacturer in Rotherham before embarking on a PhD with the University of Manchester. At the time of submission of this thesis, he was a Research Scientist with Purolite International in Wales.
It seems probable to me, that God in the beginning formed matter in solids, massy, hard, impenetrable, movable particles; ... even so very hard, as never to wear or break in pieces.

Sir Isaac Newton, Optiks London (1704)
Chapter 1: General Introduction
Chapter 1: General Introduction

Owing to its importance in a variety of applications, the determination of pore size distribution (PSD) has been a subject of extensive research in the discourse of microporous materials. Microporous materials being materials with pore widths less than 2 nm, pore widths above 2 nm up to 50 nm are called mesopores, and macropores have pore widths above 50 nm as defined by IUPAC.\(^1\) Several approaches have been used to characterise microporosity, but the most popular involves applying a selected model on gas sorption data at low pressure to obtain a pore size distribution. Other approaches include using \(^{129}\)Xe NMR and manipulating the resulting data to obtain an average pore size or pore size distribution.\(^2\) Irrespective of the approach and/or technique used, there are always uncertainties due to the concomitant assumptions made. The limited domain of applicability of a model means a model cannot be universally applied. In order to apply a model to new materials therefore, it is imperative to use independent methods to verify its efficacy, so that crystallographic techniques, NMR, and computer simulations can be used to verify models that rely on manipulating gas sorption data.

1.0 Aims and Objectives

This research is informed by the following aims and objectives:

1.0: To develop a reliable methodology for determining the distribution of pore size in microporous (i.e., pore size <2 nm) organic materials, using molecular probes such as N\(_2\) and CO\(_2\).

1.1: To establish reproducible experimental procedures for the determination of N\(_2\) and CO\(_2\) adsorption isotherms for microporous organic materials.

1.2: To apply and compare a range of theories (Horvath-Kawazoe model, Dubinin-Astakhov (DA) theory, Density Functional Theory (DFT), Barrett-Joyner-Halenda (BJH) approach, etc.) for the determination of pore size distribution from gas adsorption data.

1.3: To compare apparent pore size distributions from N\(_2\) and CO\(_2\) adsorption with data from other techniques like Xe sorption, computer simulation, \(^{129}\)Xe NMR, and positron annihilation.
2.0: To correlate H₂ adsorption data with pore size distribution data obtained as described under 1.0.

2.1: To investigate the influence of polymer structure on its gas sorption properties.

2.2. To investigate the effect of sample form (powder and membrane form) on its sorption behaviour.

3.0: To correlate CO₂ adsorption data obtained at high pressure (10 bar) with pore size distribution data obtained as described under 1.0.

3.1: To investigate the effect of the history of a PIM-1 sample on its microporosity.

4.0: To apply Attenuated Total Reflection- Fourier Transform- Infra Red spectroscopy (ATR-FT-IR) in order to elucidate the nature of the interaction between hydrogen bonding agents (water, methanol, ethanol, propanol, butanol, chloroform) with a PIM-1 membrane.

In order to achieve these objectives, the following strategy has been pursued: (i) N₂ adsorption at 77 K from low relative pressures (10⁻⁹) to obtain pore size distribution (PSD) data and demonstrate its limitations, and (ii) CO₂ adsorption at 273 K at sub-atmospheric pressures (using the volumetric method) and 303 K at high pressure (using gravimetric methods). Although PIM materials are not very similar to graphite, which has slit-pores, the Horvath-Kawazoe model, which applies to slit-pores, has been used to manipulate the data. Comparison of this model to other techniques like computer simulation was used to validate its applicability for these materials. Its application on crystalline materials also allowed corroboration with crystallographic data generated from examination of such materials. Aims on developing improved and new materials were pursued through modifying PIM-1 after synthesis and also through developing and investigating the properties of PIM-2, and characterisation of triptycenes and PIM-1 copolymers. These materials were studied mainly in powder form and, where possible, in film form as well.
1.1 Microporous materials

Microporous materials have molecular size ($\leq 2$ nm) interlinked pores.$^{1,3-5}$ These materials characteristically have large surface areas which lend them to many technological applications such as catalysis,$^{1,6,7}$ adsorption,$^{4}$ gas storage,$^{8}$ and many others. The field of microporous materials has, until recently, been dominated by zeolites and activated carbons.$^9$ Metal-organic frameworks (MOFs) research has more recently been extensively studied.$^{10-12}$ In view of the potential scope and utility of microporous materials, there is sufficient motivation in developing new materials with specific properties that are tuneable through systematic structural modifications.

1.1.3 Activated Carbons

Different forms of carbon have been used as adsorbents,$^{13,14}$ deodorisers and catalyst supports.$^{15}$ Microporosity can be induced in both natural and synthetic carbons using a wide range of methods, for example carbonisation, or chemical activation with a strong base. The resulting material can have surface areas ranging from 1000 to 3000 m$^2$ g$^{-1}$.

Like many porous materials, activated carbons are widely used in separations as adsorbents and in catalysis as metal support media.$^6$ Single-walled carbon nanotubes (SWNTs) have been inferred$^{16}$ to store 5–10 wt% of hydrogen at ambient temperature. Although later disputed, this report inspired a great deal of research into hydrogen storage using such carbon materials as graphite nanofibers, multiwalled carbon nanotubes (MWNTs) and nanographite.$^{17}$ Microporosity in carbons is due to the polymer network structure whereby a random configuration of planar graphene sheets is cross-linked by non-graphitised aliphatic units.$^9$ Owing to their method of synthesis, activated carbons do not have well-defined chemistries. Their surfaces contain a mix of oxygen- and nitrogen-containing functional groups in addition to the polycyclic aromatic units from the graphene sheets. The pore size distribution of these materials is broad with pores ranging from micropores through mesopores to macro pores. Although this limits chemoselectivity, it is useful in adsorbing a wide range of organic molecules and metal ions.
1.1.2 Zeolites

Naturally occurring and synthetic zeolites are hydrophilic aluminosilicate minerals which can be used as molecular sieves due to their ability to separate molecules selectively according to their size and geometry. They are yet another class of microporous materials with ordered crystalline structure consisting of a Al-O-Si backbone. These have the general form, $M_{n/m}(AlO_2)_x(SiO_2)_y\frac{1}{z}H_2O$ where $n$ is the charge of the metal ion, for example Na$^+$, K$^+$, or Ca$^{2+}$, and $z$ is the moles of the water of crystallisation. The metal ion charge balances the net negative charge associated with the aluminium content of the material, and for this reason zeolites are useful cationic ion exchangers. Guest molecules (the cations) must have a smaller width than the aperture of the cavity of the framework, as this aperture dictates the properties of the zeolite material.

The synthesis of zeolites involves the use of hydrothermal crystallisation with the stoichiometric ratios of reactants, reaction time and temperature determining the properties of the resulting material. The well defined structure and chemistry of zeolites allows them to be used to study the chemistry of hydrogen binding to a variety of metal cation centres. Other applications include heterogeneous catalysis, use as catalyst supports, water softening, and as additives in detergents. Their porosity gives them high surface areas. Zeolite Y has a BET surface area of $\sim 900$ m$^2$ g$^{-1}$, and is used in catalytic cracking in the separation of gasoline and octane from crude oil. A schematic illustration of zeolite A, which is a typical example, is shown in Figure 1.1.

![Figure 1.1 Structure of a Zeolite A](image)

Despite being useful for these and other applications however, zeolites are limited by their inability to accommodate guest molecules of a different dimension to the
cavity. They are also not very suitable for on-board hydrogen storage owing to the high density of the aluminosilicates framework.\textsuperscript{18}

1.1.3 Metal-Organic Frameworks (MOFs)

In contrast to the entirely inorganically constituted zeolites, metal-organic framework materials (MOFs) are formed by dative bonds from multi-dentate organic ligands to mono- or poly-nuclear metal centres.\textsuperscript{18} They usually have open-framework structures leading to the inclusion of guest molecules like solvents. If these guest molecules are removed, the resulting structure can be porous with high BET surface area.\textsuperscript{7, 20}

MOF synthesis uses hydrogen and metal-ligand coordinate bonding allowing for a vast possibility of different frameworks\textsuperscript{21} as illustrated in Figure 1.2.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.2.png}
\caption{The modular principle to building MOFs\textsuperscript{21}}
\end{figure}

Worthy of particular note is MOF-5, whose BET surface area is in the region of 3800 m\textsuperscript{2} g\textsuperscript{-1}.

Because they can be tailored in structure and functionality for particular applications, metal-organic frameworks have a great potential in such areas as
chemical catalysis, gas separation, and molecular recognition. Further applications are likely to emerge as new materials are developed. One strength of these materials is the possibility of generating unusually large diameter channels and cavities. The major limitation however, is that most of these frameworks are not intrinsically porous, that is, they are not robust enough to maintain porosity upon removal of solvents.

The permanent porosity that exists in classical rigid adsorbents is associated with the structural rigidity of the constituent bonds, for instance the Si–O bond in zeolites or C–C bond in carbon-based adsorbents. The higher thermal and chemical stability of classical adsorbents as compared to the new generation of coordination framework materials means that the latter structures must provide alternative mechanisms for adsorption/desorption to compete for use in associated applications. This is possible due to the extra internal degrees of freedom (rotation, torsion, vibration) evident in MOFs, which allows the materials to be flexible. The use of MOFs for hydrogen storage however, is severely limited by their high density, hence the motivation for developing lighter materials.

1.1.4 Covalent Organic Frameworks (COFs)

Covalent organic frameworks (COFs) have largely been developed to counter the limited stability and high densities of MOFs. These frameworks comprise mainly of light atoms (B, C and O), held together by strong covalent bonds. This means that, in addition to their low density, they are more thermally stable, and remain intact even after the removal of penetrants. This makes COFs excellent materials for hydrogen storage. An example is COF-1, which is produced by dehydration as illustrated in Figure 1.3.
Like MOFs, it is possible to tailor-make COFs by careful selection of monomers, to produce high surface areas. BET surface areas are typically around 4000 m² g⁻¹.

1.1.5 Polymers of Intrinsic Microporosity (PIMs)

PIMs are interesting because, while most polymers have flexible backbones that enable them to pack together relatively efficiently, so that they do not routinely form porous solids⁹, 25, PIMs comprise of a rigid spirobisindane based motif which impacts on the polymer chain intrasegmental mobility resulting in enhanced pore volume.²⁶ This microporosity is accessible to probe molecules like nitrogen and carbon dioxide. PIMs thus have varied potential applications, which include selective adsorption of small molecules, membrane-based gas separation, heterogeneous catalysis and, most recently, polymer electrolyte membrane (PEM) technology.

PIMs are novel network and non-network ladder polymers, initially developed at the University of Manchester. They are thermally stable materials that exhibit high surface area with microporous and ultramicroporous morphology.¹⁵, ²⁶⁻³⁴

Unlike most organic polymers, which are inherently flexible and are thus able to
deform and close any pores, PIMs are rigid, extremely contorted spirobisindane-based ladder polymers, that have essentially no rotational freedom in the polymer backbone (sites of contortion give the backbone an irregular, kinked shape). This results in large free volume as illustrated by the BET surface areas of about 800 m² g⁻¹ typically.¹ ³⁵ Although PIMs have lower surface areas than some other similar materials like hypercrosslinked polystyrene (1930 m² g⁻¹) or some hypercrosslinked resins synthesised by Lee et al.,³⁶ they are capable of storing high quantities of molecular hydrogen as a consequence of their microporosity.³⁷

The most widely studied non-network PIMs are PIM-1, PIM-7 and PIM-2. Following is a brief overview of each of these materials a more detailed treatment is presented in Chapter 2.

1.1.5.1 PIM-1

PIM-1 (Figure 1.4) was the first of the homologues of soluble polymers of intrinsic microporosity to be synthesised. The apparent microporosity is termed *intrinsic* because, although like any other glassy structure it is non-equilibrium, it is due to the molecular structure and is not an artefact of processing.³⁸ The common characteristics of a PIM are (i) no, or extremely restricted, rotational freedom about all bonds in the backbone and (ii) the presence of sites of contortion such as spiro-centres.²⁷, ³⁹ Gas permeation experiments show that PIM-1 has high permeability and selectivity above the Robeson upper bound for gas pair like O₂/N₂ and CO₂/CH₄.³³
Non-network PIMs are readily soluble in organic solvents and relatively easy to process into membranes and other forms. PIM-1 is soluble in solvents such as tetrahydrofuran and chloroform, dichloromethane, o-dichlorobenzene and acetophenone, and can be precipitated as a powder or cast from solution to form a robust permeable membrane. The synthesis of PIM-1 is described in Chapter 2.

1.1.5.2 PIM-7

PIM-7 (Figure 1.5) differs from PIM-1 in that, whereas PIM-1 uses 2,3,5,6-tetrachloroterephthalonitrile (TCTPN) or 2,3,5,6-tetrafluoroterephthalonitrile (TFTPN) to react with bis-5,5',6,6'-tetrahydroxy-3,3',3'-tetramethyl-1,1'-sporobisindane A, PIM-7 uses 7,7',8,8'-tetrachloro-3,3',3'-tetramethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[cyclopenta[b]phenazine]. This is consequently reflected in the differences in structure of the resulting polymer repeat units. In PIM-7, for example, the phenazine unit has been used as a ligand for the coordination of metal ions and a PIM-7 membrane is readily crosslinked with Pd(II) salts. 

Figure 1.4 (a) The structure of PIM-1 (b) Representation of the PIM-1 repeat unit using Van-der-Waals spheres.
Figure 1.5 The structure of PIM-7.

1.1.5.3 PIM-2

PIM-2 (Figure 1.6) is a non-network polymer made from bis-5,5′,6,6′-Tetrahydroxy-3,3,3′,3′-tetramethyl-1,1′-sporobisindane A and decfluorobiphenyl (DFPB). Because of the high surface area and the presence of interconnected pores, PIM-2 has a high free volume and hence high vapour permeation rate. The elevated vapour permeation rates could make it useful for vapour sensing. In this respect PIM-2 offers great potential since it is white and soluble in aprotic polar solvents and thus can be processed into films which easily incorporate fluorescent dyes that are sensitive to certain molecules, for example Nile Red has been used to sense ethanol vapours. Other uses of PIM-2 might be in forming membranes that can be used in CO₂ capture. There is a lot of scope in blending with other PIMs like PIM-1 to give membranes with hybrid and, hopefully desired characteristics.

Figure 1.6 The structure of PIM-2.
One limitation of PIMs is that the pore size distribution is often broad and difficult to control or tune. This shortfall however, is outweighed by the high surface areas, large pore volumes, and the possibility of incorporating functional groups. Organic materials such as polymers offer a significant weight advantage, particularly over metal-based materials, because they comprise only of relatively light elements (e.g., C, H, N, O). This is particularly important in the transport industry where weight considerations are of great significance. Thus PIMs can be regarded as organic analogues of zeolites; zeolites themselves being prototypic ordered nanoporous materials. Not only are there a number of well-developed ways of synthesising organic polymers with desirable chemical and mechanical properties, but also the chemical functionalities and structural topologies of these materials can be easily varied.

1.2 Potential Applications of Porous Materials

1.2.1 The hydrogen economy

Because fossil fuel reserves are diminishing, there is a need to decrease the worldwide dependency on petroleum products as a source of vehicular fuel. The use of molecular hydrogen (H₂) as a fuel for transport would allay the problems of rapidly declining levels of oil and concerns about the effects of increasing levels of atmospheric CO₂ on the climate. For this to be a real advantage the hydrogen needs to be produced by environmental friendly means rather than through the current process of steam reforming of natural gas. In this respect the hydrogen economy is an option with great promise. Before hydrogen can be available for wide vehicular use however, safe, compact, and high capacity storage systems for molecular hydrogen need to be developed. To this end, the U.S. Department of Energy (DOE) set a target for the development of materials capable of storing 9wt % of hydrogen by the year 2015. Hydrogen storage methods to-date are energy intensive so they require further development for use at ambient temperatures and relatively low pressure. The constraints materials for hydrogen storage also have to satisfy include reasonable volume, light-weight, and practical kinetics for charging and discharging of the gas. The light weight allows the materials to have a low density and hence adsorb higher weight percentage of hydrogen.

Hydrogen storage technology is one of the key technologies for the Hydrogen economy. A range of materials, including carbon nanotubes, metal hydrides,
zeolites and metal-organic frameworks\textsuperscript{12, 36, 43}, has been studied as adsorbents for H\textsubscript{2}. Modified IRMOF-8 can store up to 4 \% w/w H\textsubscript{2} at room temperature and 100 atmospheres.\textsuperscript{44} Storing large quantities of hydrogen in the limited space of a motor vehicle remains a major challenge that is yet to be overcome.\textsuperscript{45} Possible ways of storing hydrogen as a fuel in an automobile include liquid hydrogen at low temperature (typically <20 K), compressed gaseous hydrogen (ca. 700 Bar), atomistic hydrogen in the form of metal hydrides, or adsorption in microporous materials.\textsuperscript{16}

1.2.1.1 Hydrogen storage as a compressed gas

The current benchmark system for hydrogen storage in cars uses compressed hydrogen at 700 bar. This system is both conceptually fairly simple and technically feasible. High-pressure compression of gaseous hydrogen however, takes up large volumes of space (1 kg of hydrogen at 700 bar occupies 27 litres) and requires a rigorous design of storage tanks, such as multiple layers to avoid rupture, and cylindrical geometry which does not readily fit into an existing vehicle design. Figure 1.7 shows the profile diagram of a compressed hydrogen gas storage tank.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{compressed_hydrogen_gas_storage_tank.png}
\caption{A compressed hydrogen gas storage tank.} \textsuperscript{42}
\end{figure}

The inner lining of the compressed hydrogen gas tank is made of high molecular weight polymer that acts as a permeation barrier. A carbon fibre-epoxy resin composite shell is placed over the liner and constitutes the gas pressure, load
bearing component of the tank. Then, an outer shell protects the tank from impact.

1.2.1.2 Hydrogen storage as a liquid

Keeping hydrogen as a liquid requires cryogenic temperatures. Because hydrogen vaporises at 20 K, a super insulated cryogenic tank is required (Figure 1.68. This however, comes with the problems of hydrogen boil-off due to thermal conduction through the plumbing system, resulting in the tank emptying itself within a few days of being idle. There are also cooling losses during refuelling, so that the piping system must be cooled to cryogenic temperatures before refuelling. In addition, the high energy required to liquefy hydrogen is prohibitive. The volume, weight and cost of the tank are also high.

Figure 1.8 A liquid hydrogen fuel tank.

1.2.1.3 Hydrogen storage by chemisorption in metal hydrides

Metal hydrides have the potential for reversible hydrogen storage and release (in the presence of another reactant or under suitable conditions of temperature and pressure) at low temperatures and pressures (Equation 1.1). Such materials can be used either for reversible hydrogen storage so that they can be reloaded with H₂ as required, or as irreversible storage media that require replacement on exhaustion.

\[
M + H_2 \rightleftharpoons MH + \Delta H \quad (1.1)
\]
A simple metal hydride such as lanthanum nickel hydride (LaNi$_5$H$_6$), which incorporates hydrogen into its crystal structure, can function in the pressure-temperature range of 1 – 10 atm and 298 - 393 K, but its gravimetric capacity is too low (only approximately 1.4 wt.%) which means 360 kg of LaNi$_5$H$_6$ will store only about 5 kg of H$_2$. In addition, its cost is too high for vehicular applications.

Complex metal hydrides such as alanate (AlH$_4$) materials have the potential for higher gravimetric hydrogen capacities in the operational window than simple metal hydrides. Other hydrides, like MgH$_2$ have considerably high capacity (7.6 wt. %), but the hydrogen is too strongly bound to the metal.

Although metal hydride systems have fairly good safety characteristics and have a high capacity for hydrogen, the disadvantages are that, being metal based, these systems are heavy and metal hydrides require high temperatures of dissociation and therefore a high energy input.

1.2.1.4 Hydrogen storage by physiosorption in microporous materials

Hydrogen storage in porous materials at low temperature (77 – 100 K) offers some advantages over the other methods in terms of the size and weight, the challenge however, is how to store useful quantity of hydrogen in porous materials under moderate conditions.

For PIMs the highest hydrogen storage capacity observed so far is 2.7 % at 10 bar and 77 K by a triptycene based PIM (more information of Triptycene PIMs is presented in Chapter 2). Activated carbons have been reported to have achieved 4 % under the same conditions of temperature and pressure, and MOFs achieved 3.7 %. Clearly, none of these materials meets the current criteria of size, storage capacity, recharge kinetics, cost, and safety required for application in transportation systems.

1.2.2 Other Applications

The use of microporous material in methane storage applications has also been investigated. Materials such as hypercrosslinked polystyrene and some MOFs have been examined. Other applications of microporous materials include heterogeneous catalysis, use in organic light emitting diodes (OLEDs), and selectively permeable membranes.
Because of their low dielectric constant and structural rigidity, polymers containing the triptycene unit have been used in the manufacture of faster integrated circuits.\(^{49}\) With a pore diameter in the range 0.4 – 1.5 nm, zeolites find application as molecular sieves. The ease with which they can be functionalised using different moieties means they can be used as ion exchangers. Probably the biggest application for zeolites is in catalysis. Activated carbons can be used for liquid phase applications like water purification and decolorising. Their gas phase applications include solvent recovery, air purification, gasoline recovery and catalysis.
1.3 Scope of the Thesis

Chapter 2 describes the synthesis of PIMs. It also describes other materials obtained from elsewhere and used in this research. Characterisation techniques, namely $^1$H NMR, MALDI-TOF and Elemental analysis, are also included. N$_2$ sorption data at 77 K for the materials is presented and discussed.

Chapter 3 begins with presenting models for determining pore size distributions. The strengths and limitations of each model is discussed and applied to different materials. Various pore size distribution models are discussed and justification for relying on the Horvath-Kawazoe model presented. The gas sorption methodology is validated before being applied. Gas sorption data for PIM-1, PIM-2, PIM-7, 3,3',4,4'-tetra(trimethylsilylethynyl)biphenyl (the organic crystal), triptycene-based PIMs, ethano-anthracene PIM-1 copolymers, and PIM-1 films using CO$_2$ (273 K), CO$_2$ (303 K), and N$_2$ (77 K) are presented. These data are used to compare different pore size distribution models, investigate the influence of structure and sample form on gas sorption behaviour.

Chapter 4 presents Xe and N$_2$ sorption, and Positron annihilation lifetime spectroscopy (PALS) studies on PIM-1 and ethano-anthracene PIM-1 copolymer. The data is used to investigate the influence of the history of a polymer sample on its sorption properties, and to investigate the aging of polymer powders and membranes.

Chapter 5 is a study of the interaction of PIMs with penetrants in the liquid and vapour form. This interaction is largely hydrogen bonding (HB). ATR-FT-IR data for PIM-1 membranes before and after treatment with various hydrogen bonding agents (water, methanol, ethanol, propanol, butanol, phenol, and chloroform) is presented and analysed.

Chapter 6 gives the overall conclusions for the research.
Chapter 2: Materials
Chapter 2: Materials

2.0 Introduction

This chapter presents the theory of step-growth polymerisation and its application in the synthesis of PIMs. The synthesis of PIM-1, TAPIM-1, PIM-2 and PIM-7 is then described. A brief overview of materials subsequently studied in Chapters 3 and 4 but obtained from other sources is also presented.

2.1 Step-growth polymerisation

PIMs are synthesised via polycondensation step polymerisation reactions, eliminating small molecules as the reaction progresses. These involve multifunctional monomers reacting to give dimers, trimers, long chain oligomers, and subsequently high molecular weight polymers. The functionality \( f \) is the number of functional groups present on a monomer. For successful polymerisation \( f \) must be at least 2. To get a linear polymer, \( f \) must be 2, otherwise branching and/or cross-linking results. For a high molecular weight polymer, the extent of reaction must be as close to completion as possible. To achieve this, stoichiometric control is pivotal. Disproportionate quantities can result in shorter polymer chains. The variation of molecular weight with conversion rate is shown in Figure 2.1.

![Figure 2.1: Dependence of degree of polymerisation on the extent of reaction in step-growth polymerisation, according to Carother’s theory (Equation 2.4).](image-url)
Carothers theory\textsuperscript{50} has been used to predict the molar mass of polymer prepared via step polymerisation. This makes use of the relationship between the number of molecules present at the start of the reaction, $N_o$, and the number of molecules present at time $t$, $N$, to the number average degree of polymerisation $\bar{x}$ as shown in Equation 2.1.

$$\bar{x}_n = \frac{N_o}{N} \quad (2.1)$$

If the monomer stoichiometric ratio is 1:1, then $\bar{x}_n$ can be related to the extent of reaction, $p$, by Equation 2.2.

$$p = \frac{f_r}{f_o} \quad (2.2)$$

Where $f_r$ is the number of functional groups that have reacted, and $f_o$ is the number initially present. Thus $p$ represents the probability that a functional group initially present has reacted. For each reaction between pairs of functional groups the total number of molecules present will decrease by one, therefore Equation 2.2 can be written as:

$$\frac{N_o}{N} = \frac{1}{1-p} \quad (2.3)$$

Which, on substituting in $\bar{x}_n$ gives the Carothers equation:

$$\bar{x}_n = \frac{1}{1-p} \quad (2.4)$$

It is therefore important to have $p \geq 0.99$ (as shown in Figure 2.1) in order to produce a high molecular weight polymer. This demonstrates the need for monomer purity, efficiency, and strict stoichiometry control. For PIMs, the number average molecular weight, $\bar{M}_n$, can be used as a measure of reaction success. Equation 2.5 shows how this is related to $\bar{x}_n$.

$$\bar{M}_n = \bar{M}_o \times \bar{x}_n \quad (2.5)$$

Where $\bar{M}_o$ is the average molar mass of the monomer unit.

$$p = \text{molar mass of repeat unit} / \text{number of monomers in repeat unit} \quad (2.6)$$
The weight average molecular weight, $\overline{M}_w$, can also be used as an indicator of polymerisation success. Its relationship with $p$ is given by Equation 2.7.

$$\overline{M}_w = \overline{M}_o \frac{(1 + p)}{1 - p}$$ (2.7)

Giving:

$$\bar{\omega}_w = \frac{(1 + p)}{(1 - p)}$$ (2.8)

As $p$ approaches 1 (complete conversion), $\bar{\omega}_w$ approaches infinity.

The polydispersity index, $\overline{M}_w / \overline{M}_n$, is the molecular weight distribution for a given sample.

$$\frac{\overline{M}_w}{\overline{M}_n} = 1 + p$$ (2.9)

For linear step polymerisation this value is usually around 2, and high $p$ values are required.\(^{51}\)

### 2.1.1 PIM-1

The synthesis strategies for PIM-1 used by Budd et al.\(^{28, 39}\) involved step polymerisation, which utilises the remarkably efficient double aromatic nucleophilic substitution (i.e., dioxane-forming reaction) between a bi-functional aromatic monomer bearing multiple hydroxyl groups, 5,5′,6,6′-tetrahydroxy, 3,3′,3′-tetramethyl-1,1′-spirobisindane (bis-5,5′,6,6′-Tetrahydroxy-3,3′,3′-tetramethyl-1,1′-spirobisindane A) and another bi-functional aromatic monomer bearing multiple fluorines, 2,3,5,6-tetrafluoroterephthalonitrile (TFTPN), or chlorines, 2,3,5,6-tetrachloroterephthalonitrile (TCTPN) (Figure 2.2). To obtain an intrinsically microporous polymer, at least one of the monomers must contain a site of contortion such as a spiro-centre (an sp\(^3\) carbon which is part of two five-membered rings), a non-planar rigid skeleton, or a single covalent bond about which rotation is severely hindered. In the case of PIM-1, high molar mass polymer is readily obtained at temperatures in the range 60–80 °C, but the molar mass is reduced at higher temperature.\(^{18}\)
2.1.2 Post-synthetic Modification of PIM-1

A range of methods have been employed for the chemical modification of aromatic polymers such as polyetheretherketones (PEEK) and polysulfone (PSF). Sulphonation, for instance, has been carried out using sulphuric acid or chlorosulphonic acid$^{52,53}$ and by a method involving lithiation, SO$_2$ treatment then oxidation. Post-synthetic modification of PIM-1 is aimed at introducing desired functionalities to engineer certain properties into the material. Being hydrophobic, PIM-1 is limited in some applications such as in fuel cell membranes and the removal of metals from aqueous solution.
2.1.2.1 Thioamide PIM-1 (TAPIM-1)

Introducing S groups to the PIM-1 repeat unit is likely to improve its solubility in polar solvents and also make it potentially able to react with metals. This can be useful in catalysis and in the removal of heavy metals from aqueous systems,\textsuperscript{54, 55} for example.

Thionation is the most efficient method for the synthesis of organosulphur compounds.\textsuperscript{56} A number of different thionating techniques have been reported. The use of tetraphosphorus decasulphide ($P_4S_{10}$) as a thionating reagent for converting carbonyls to thiocarbonyls is well documented.\textsuperscript{34, 56-58} $P_4S_{10}$ is a versatile reagent widely available as a yellow crystalline solid that decomposes upon exposure to moisture. Synthesis of primary thioamides using sodium trimethylsilyl sulphide in 1,3-dimethyl-2-imidazolidinone has been reported\textsuperscript{59}. Goswami et al.\textsuperscript{34} described a rapid exothermic reaction through which aliphatic, aromatic and heterocyclic nitriles can be thionated to give the corresponding thioamides using phosphorus pentasulphide and sodium sulphite at room temperature. The same reaction can also be carried out under microwave-assisted conditions,\textsuperscript{60} although this method does not give good yields. The reaction of nitriles with phosphorous pentasulphide at room temperature can be performed in polar solvents like acetonitrile or tetrahydrofuran (THF) in the presence of a base catalyst.\textsuperscript{57} The adapted reaction scheme for PIM-1 would be as shown in Figure 2.3.
Goswami et al.\textsuperscript{34} proposed a reaction mechanism where phosphorus pentasulphide and sodium sulphite react to generate the thionating nucleophile either by reducing the weak P=S bond or by reductive cleavage of the P-S bond of P$_4$S$_{10}$, since P$_2$S$_5$ exists as tetraphosphorus decasulphide, P$_4$S$_{10}$ (Figure 2.4, step 1). The nascent nucleophile so generated attacks the electrophilic bond of the cyano group resulting in the thioamide after an aqueous work-up (Fig. 2.4, step 2). The aqueous work-up liberates the thioamide by nucleophilic attack by water on the pentacoordinated phosphorus intermediate, I. This is then followed by tautomeric shift of hydrogen from the sulphur atom to the nitrogen atom. Sodium sulphite serves to facilitate the rapid release of the nucleophile PS$_3^-$ to form I.

\textit{Step 1. Generation of the thionating nucleophile}

\[ \text{P}_2\text{S}_5 + 2 \text{Na}_2\text{SO}_3 \rightarrow 2 \text{PS}_3^-\text{Na}^+ + \text{SO}_2 + 2 \text{O}_2 \]

\textit{Step 2. Aqueous work-up.}
In order to obtain the degree of thionation, the average number of thionitriles per repeat unit is determined using ¹HNMR, but this can only be used as an estimate.

**2.1.3 PIM-2**

PIMs are generally prepared from appropriate rigid monomers. A requirement for microporosity is the presence of a site of contortion from at least one such monomer. This site of contortion may be a spirocentre, or a single covalent bond around which rotation is hindered, as in the di-reactive decafluorobiphenyl (DFBP) (Figure 2.5). Sometimes a non-planar rigid framework is sufficient. The lack of rotational freedom along the polymer backbone prohibits efficient packing and hence results in high free volume and microporosity. A PIM made from 5,5',6,6'-Tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-sporobisindane A and DFPB is called PIM-2, which is a white free flowing powder. Like PIM-1, PIM-2 is a non-network soluble polymer which can potentially be processed into membranes. Because of the available fluorine atoms, however, there is likelihood that PIM-2 will form a network or perhaps crosslink more readily. The reaction scheme for the synthesis of PIM-2 is shown in Figure 2.5 below.
Figure 2.5 The reaction scheme for the synthesis of PIM-2 (using 5,5',6,6'-Tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-sporobisindane A and DFBP monomers).

2.1.4 PIM-7

PIM-7 is prepared in a number of stages. These involve preparation of one of the monomers, tetrachloromonomer from the 5,5',6,6'-Tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-sporobisindane via the tetraketone. The tetrachloromonomer is then subsequently reacted with 5,5',6,6'-Tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-sporobisindane-A to give PIM-7 (Figure 2.6). The details of each stage are outlined in section 2.4.4.
Figure 2.6: The reaction of the tetrachloro monomer with 5,5',6,6'-tetrahydroxy-3,3',3'-tetramethyl-1,1'-sporobisindane-A to make PIM-7.
2.2 Summary of syntheses

The synthesis of PIMs is carried out using dibenzodioxane formation between 5,5’,6,6’-tetrahydroxy-3,3,3’,3’-tetramethyl-1,1’-sporobisindane- and o-difluorobenzene containing monomers to form the fused ring linkage. This can be summarised by the illustration in Figure 2.7 below. For PIM-7, once the tetrachloro monomer has been synthesised, its subsequent reaction with 5,5’,6,6’-tetrahydroxy-3,3,3’,3’-tetramethyl-1,1’-sporobisindane-A also follows the same general scheme.

![Dibenzodioxane forming reaction used in the preparation of PIMs. X can be Cl or F. Reagents and conditions, i Monomer A, Monomer B, K₂CO₃, DMF. The red bit represents 5,5’,6,6’-Tetrahydroxy-3,3,3’,3’-tetramethyl-1,1’-sporobisindane-A, and the blue one represents TFPN, TCPN or the tetrachloromonomer in the case of PIM-7.](image-url)
2.3 Materials obtained from elsewhere

2.3.1 PIM-1 copolymers incorporating ethano-anthracene units

PIM-1 ethano-anthracene copolymers are materials in which a proportion of the spiro-units of PIM-1 are replaced by units derived from 9,10-dimethyl-9,10-dihydro-9,10-ethanoanthracene-2,3,6,7-tetrol (CO1) (Figure 2.8).

![Reaction scheme for PIM-1 ethano-anthracene copolymers](image)

**Figure 2.8 Reaction scheme for PIM-1 ethano-anthracene copolymers**

Partial replacement of the PIM-1 spiro-centres with a more rigid moiety should yield a material with different properties. This should be accompanied by changes in free volume and give an insight into the generation and stabilisation of free volume. A study of PIM1-CO1-40 sorption and $^{129}$Xe NMR measurements is presented in Chapter 4.
2.3.2 Triptycene based PIMs (TripPIMs)

TripPIMs constitute a homologous series of novel triptycene-based network polymers of intrinsic microporosity with a rigid, fused ring skeleton and three-fold symmetry (Figure 2.8).\textsuperscript{32, 37} In these materials, the BET surface area can be controlled by the length and branching of the alkyl (R) chains. The first in this series to be synthesised, i.e. when R is Ethyl has been shown to have a surface area over 1000 m\(^2\) g\(^{-1}\) and to reversibly adsorb 1.83 % hydrogen by mass\textsuperscript{32} at 1 bar/77 K and 3.4 % at 10 bar/77 K. Triptycenes combine the concept of network polymers with that of PIMs, thus microporosity and H\(_2\) carrying capacity is expected to be greater. Triptycene is an interesting structural building block for PIMs owing to its rigid, fused-ring skeleton and three-fold symmetrical structure.\textsuperscript{5} Its distinct shape results in ‘internal molecular free volume’ as put forward by Swager et al.\textsuperscript{49} This suggests that the geometry of the Triptycene unit defines a significant amount of free space.\textsuperscript{69} Triptycene derivatives can be incorporated into a PIM network. For instance, 9,10-dialkyl-2,3,6,7,12,13-hexahydroxytriptycene, which is easily prepared via the Diels–Alder reaction\textsuperscript{69} between 9,10-dialkyl-2,3,6,7-tetramethoxyanthracene and 4,5-dimethoxybenzylene (which in turn is prepared in-situ from 4,5-dimethoxyanthralinic acid), followed by BBr\(_3\) demethylation of the triptycene product. The reaction between the 9,10-diethyl-2,3,6,7,12,13-hexahydroxytriptycene and 2,3,5,6-tetrafluoroterephthalonitrile is the polymerisation reaction which gives the Ethyl triptycene network PIM (EtTripPIM). The general reaction scheme is outlined in Figure 2.9 below.
Sorption of Gases and Liquids by Polymers of Intrinsic Microporosity (PIMs)

Figure 2.9 Synthesis of TripPIMs. Reagents and conditions\textsuperscript{32}: (i) K\textsubscript{2}CO\textsubscript{3}, DMF, 80 °C.

The high microporosity relative to PIM-1, PIM-2 and PIM-7 is due to the macromolecular paddlewheel configuration of the framework, which minimises interactions between the protruding planar struts of the rigid framework and hence frustrate efficient packing.

2.3.3 3,3′,4,4′-tetra(trimethylsilylethynyl)biphenyl (Organic Crystal)

To experimentally get an insight into the scope and limitations of the Horvath-Kawazoe model, a material with a well defined crystalline structure was studied.\textsuperscript{70}

Adsorption studies on low molar mass organic crystals that exhibit microporosity by providing accessible internal surface areas has aroused considerable interest of late. Hopefully, in the long run, such crystals will provide alternative materials for a variety of applications that might include gas separations, capture and storage. While crystallinity is not a necessity for microporosity, regular crystalline structures possess considerable aesthetic appeal. For example, 3,3′,4,4′-tetra(trimethylsilylethynyl)biphenyl is especially intriguing because its apparent microporous structure has a striking similarity to that of a zeolite. The crystal has cubic symmetry, belonging to the space group \textit{pnn} and has a large unit cell (\(a = 2.958\) nm) containing 24 molecules (Figure 2.10). The calculated density of the crystal is 0.830 g ml\(^{-1}\), which is less than that expected for an efficiently
packed crystal comprising of an aromatic compound. It appears the crystal possesses a network of 0.4 nm minimum diameter open channels leading to 1.1 nm maximum diameter interconnected voids, which is superficially comparable to the pore structure of zeolite A. The source, code name and batch numbers for each material studied is summarised in Table 2.1.

Because organic crystals are only recent additions to the scope of potential hydrogen storage materials, it is therefore interesting to compare the initial data obtained against the best results obtained for other types of high surface area materials like PIMs.

**Figure 2.10. Structure of 3,3',4,4'-Tetra(Trimethylsilylethynyl)biphenyl**

The source, code name and batch numbers for each material studied is summarised in Table 2.1.
### Table 2.1: List and sources of materials studied

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<thead>
<tr>
<th>Material</th>
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<th>Source/supplier</th>
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<td>JDS057</td>
<td>Self, James Selbie*</td>
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<td></td>
<td>CT/02/07</td>
<td>Carin Tattershall*</td>
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<tr>
<td>TAPIM-1</td>
<td>PBCM35</td>
<td>Self, Chris Mason*</td>
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<td>Self</td>
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<td>PIM-7</td>
<td>CZ3</td>
<td>Self</td>
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<td>Kadhum Msayib**</td>
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<td>MeTripPIM</td>
<td>BD107</td>
<td>Badder Ghanem**</td>
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<td><strong>PIM-1 copolymers</strong></td>
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<td>KH39</td>
<td>Detlev Fritsch &amp; Kathleen Heinrich***</td>
</tr>
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<td>PIM1-CO1-50</td>
<td>KH40</td>
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<td>PIM1-CO1-61</td>
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<td>PIM1-CO1-100</td>
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<tr>
<td><strong>Organic crystal</strong></td>
<td>KJM30R5</td>
<td>Kadhum Msayib</td>
</tr>
</tbody>
</table>

* Colleagues in Prof. P. M. Budd’s research group. **Researchers in Prof. Neil McKeown’s research group, University of Cardiff. *** Researchers at Helmholtz-Zentrum Geesthacht (Centre for Materials and Coastal Research) formerly GKSS. † This is 3,3',4,4''-tra(Trimethylsilyl)ethynyl)biphenyl.
2.4 Experimental

All glassware was oven dried at 100 °C overnight before use, and solvents like DMF (for synthesis), chloroform and THF (for film casting), were distilled and desiccated with molecular sieve 4A before use.

2.4.1 PIM-1

2.4.1.1 Purification of monomers

(a) 3,3',3',3'-tetramethyl-1-spirobisindane-5,5',6,6'-tetrol

3,3',3',3'-tetramethyl-1-spirobisindane-5,5',6,6'-tetrol (20.5 g) (Alfa Aesar) was heated in MeOH (400 ml) to the point of reflux (the solid had completely dissolved before the reflux temperature has been reached). The solvent was then reduced to 50 % volume by evaporation, after which DCM (300 ml) (Sigma Aldrich) was added slowly whilst the reaction mixture was still hot. The flask was then removed from the heat and allowed to cool for ~2 h. The white precipitate that formed was then isolated by vacuum filtration and left to dry overnight. The purified product was still off-white in colouring and so the re-crystallization steps were repeated. This gave a pure white monomer 2 (11.96 g, 58 % yield).

(b) TFTPN

Methanol (Sigma Aldrich) was added to a conical flask containing TFTPN (21.14 g) (Sigma Aldrich) and heated to reflux until the monomer had completely dissolved (~120 ml). The solvent was then reduced in volume by evaporation until the solid began to precipitate out. The solution was then removed from the heat to cool and the precipitate was collected by vacuum filtration. It was then washed with a small portion of acetone (~10 ml) and dried in a vacuum desicator over P₂O₅ over the weekend to yield a white crystalline solid (13.22 g, 62.5 % yield).
2.4.1.2 Polymerisation

5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-sporobisindane (3.40 g, 9.99 mmol) TFTPN (2.00 g, 9.99 mmol) and anhydrous DMF (65 cm$^3$) (Sigma Aldrich) were heated under N$_2$ with stirring to 65 °C. After allowing the monomers to equilibrate to temperature K$_2$CO$_3$ (11.05 g, 79.96 mmol) (Fischer Scientific) was added. The reaction was stirred under an atmosphere of dry N$_2$ at 65 °C for a further 96 hours. The reaction mixture was allowed to cool and added to an excess of distilled water (650 cm$^3$) and stirred for an hour. The crude product was then collected by vacuum filtration and washed with distilled water (325 cm$^3$) and acetone (650 cm$^3$) (Sigma Aldrich), then dried in a vacuum oven at 100 °C. The yield was 4.45 g (96.74%).

2.4.1.3 Purification

The crude product was precipitated into a non-solvent as follows. A solution of PIM-1 (4.45 g) in THF (184 cm$^3$) (Sigma Aldrich) was prepared and then filtered through glass wool and added drop-wise to a stirred acetone (368 cm$^3$) and THF (184 cm$^3$) solution and stirred for an hour. The product was collected by vacuum filtration, washed with acetone (to remove oligomers) and dried in a vacuum oven at 100 °C. Pure PIM-1 of mass 3.06g (66.52%) was recovered. $^1$H-NMR characterisation (400 MHz, CDCl$_3$) gave \( \delta = 1.5\) - 1.58 (12 H, br, m), 2.01 - 2.53 (4 H, br, d), 6.51 (2 H, br, aromatic), 7.01 (2 H, br, aromatic). Elemental analysis gave C, 72.88 %, H, 4.22 %, N, 5.83 % (C$_{29}$H$_{20}$O$_4$N$_2$ requires C, 75.53 %, H, 4.39 %, N, 6.09 %). A BET surface area (powder, N$_2$ adsorption) of 720 m$^2$ g$^{-1}$ was obtained.

2.4.2 Thioamide PIM-1 (TAPIM-1)

To a one neck 500-ml round-bottomed flask was added sodium sulphite (131 mg, 1.04 mmol), phosphorus pentasulphide (463 mg, 1.04 mmol) (Fischer Scientific) and ethanol (5 ml) (Sigma Aldrich). This was allowed to stir for 1 hour after which time a white precipitate could be seen. (Cooling with ice-water was required as reaction became warm). To the mixture was added 1,4-dioxane (40 ml) and PIM-1 (120 mg, 0.26 mmol). This was allowed to stir for a further 1 hour before setting to reflux for 20 hours. The mixture was then cooled and deionised water (40 ml) added. This was stirred for a further 2 hours before a 1:1 (v/v) CHCl$_3$/THF mixture (40 ml) was added. The organic phase was removed and
washed with brine (2x50 ml) and dried with MgSO₄ (Fischer Scientific). Using the rotary evaporator, the solvents were then reduced in volume and the polymer precipitated with hexane. After filtering, the polymer was re-dissolved in minimal THF, and the solvent volume reduced again. Thereafter, the polymer was again precipitated with hexane. A further purification by stirring in hot methanol (10 ml) for 1 hour before allowing to cool and collecting by filtration was done. This was then dried in a vacuum oven overnight to give a slightly orange solid (1.02 g).

Characterisation of the resulting product was done by ¹H-NMR (400 MHz, DMSO) gave δ_H 1.0-1.8 (12 H, br, m), 2.0-2.2 (4 H, br, d), 6.2 (2 H, br, aromatic), 7.2 (2 H, br, aromatic), 9.8-10.2 (4 H, br, amine). Elemental analysis gave C, 66.3 %, H, 5.2 %, N, 4.6 %, S, 8.4 % (C₂₉H₂₄N₂S₂O₄ requires C, 70.1 %, H, 4.5 %, N, 5.6 %, S, 6.9 %) and an estimation of the residual amounts of phosphorus was done using Elemental Analysis. From the IR spectrum, the absence of a peak in the region 2260-2200 cm⁻¹ indicates the nitriles have been converted, and the peak around 1600 cm⁻¹ indicates the presence of NH₂ groups. A BET surface area (powder, N₂ adsorption) of 410 m² g⁻¹ was obtained.

**2.4.3 PIM-2**

Before synthesis, monomers were purified as in section 2.4.1.3. Instead of TFTPN, DFBP (Alfa Aesar) was used. A mixture of anhydrous potassium carbonate (1.243 g, 9.0 mmol), 3,3,3',3'-tetramethyl-1-spirobisindane-5,5',6,6'-tetrol (1.02 g, 3.0 mmol) and 2,2',3,3',4,4',6,6'-decafluorobiphenyl (DFBP) (1.00 g, 3.0 mmol) in dry DMF (100 ml) was stirred at 120 °C for 5 h. The mixture was cooled and added to water (300 ml) and the product collected by filtration. The crude product was purified by repeated precipitation from THF solution into methanol and subsequently filtered to yield 1.48 g (83 % yield) of a white solid. The white product was vacuum dried for at least 8 h before characterisation and film casting. Elemental analysis gave C, 65.3 %; H, 3.59 %; F, analysis not available. C₃₃H₂₀F₆O₄ gives C, 66.67 %, H, 3.39 %, F, 19.17 %; ¹HNMR (400 MHz, CDCl₃) gave δ_H 1.2-1.5 (12 H, br, m) 2.15-2.5 (4 H, br, m) 6.5 (2 H, br, s) 6.8 (2 H, br, s); and BET Surface area (powder, N₂ adsorption, Coulter 3100) was 550 m² g⁻¹.
2.4.4 PIM-7

The stages involved in PIM-7 preparation are:

Stage 1: Oxidation of 5,5′,6,6′-Tetrahydroxy-3,3,3′,3′-tetramethyl-1,1′-sporobisindane
Stage 2: Purification of the dichloro-diamine
Stage 3: Reacting the dichloro-diamine with the tetraketone made in stage 1
Stage 4: Purification of the tetrachloromonomer
Stage 5: Polymerisation of tetrachloromonomer and 5,5′,6,6′-Tetrahydroxy-3,3,3′,3′-tetramethyl-1,1′-sporobisindane
Stage 6: Purification of PIM-7 by precipitation into non-solvent.

Following is a more detailed description of how each of these stages was carried out.

Stage 1: Oxidation of 5,5′,6,6′-Tetrahydroxy-3,3,3′,3′-tetramethyl-1,1′-sporobisindane (Figure 2.11).

![Oxidation of 5,5′,6,6′-Tetrahydroxy-3,3,3′,3′-tetramethyl-1,1′-sporobisindane](image)

**Figure 2.11 Oxidation of 5,5′,6,6′-Tetrahydroxy-3,3,3′,3′-tetramethyl-1,1′-sporobisindane to form the tetraketone (RT stands for room temperature).**

Solutions of 5,5′,6,6′-Tetrahydroxy-3,3,3′,3′-tetramethyl-1,1′-sporobisindane (4.00 g, 11.7 mmol) in acetonitrile (100 cm³) (Sigma Aldrich) and ammonium cerium (IV) nitrate (50.50 g, 94.0 mmol) (Alfa Aesar) in deionised water (100 cm³) were prepared. The ammonium cerium (IV) nitrate solution was stirred for a further 2 hours at room temperature and the product collected by vacuum filtration and washed with ethanol. The resulting tetraketone was then dried.
overnight at 100 °C to give a yield of 3.16 g (79.90%). Characterisation with \(^1\)H-
NMR (400 MHz, CDCl\(_3\)) gave \(\delta_{\text{H}}\) 1.4 (12 H, br m, CH\(_3\)), 2.4 (4 H, br, CH\(_2\)), and 
6.3 (4 H, br, aromatic). Elemental analysis gave C, 75 %, and O, 6 %. ATR-FT-IR 
analysis gave a stretch at 1650 cm\(^{-1}\), signifying the presence of the C=O group, 
and the absence of peaks in the regions 3200 – 3600 cm\(^{-1}\) indicated the absence 
of the OH group.

Stage 2: Purification of the dichloro-diamine (Figure 2.12).

Figure 2.12 Structure of the dichloro-diamine.

Dichloro-diamine (10.00 g, 56.5 mmol) was added to hot ethanol (400 cm\(^3\)) with 
stirring. Dichloro-diamine solution was filtered through filter paper and added to 
distilled water (2 000 cm\(^3\)). The product was collected by vacuum filtration and 
dried overnight at room temperature, taking care not to expose the product to 
light. A yield of 6.65 g (65.57 %) was obtained.

Stage 3: Reacting the dichloroamine with the tetraketone (Figure 2.13).

Figure 2.13 Reaction of the tetraketone with the dichloro-diamine to 
make the tetrachloro monomer.

Tetraketone (3.00 g, 8.92 mmol), purified dichloro-diamine (6.32 g, 35.70 
mmol), and acetic acid (180 cm\(^3\)) were refluxed under N\(_2\) at 120 °C for 3 hours.
The product was collected by vacuum filtration and washed with acetic acid, distilled water and ethanol. The yield was 4.69 g (84 %).

Stage 4: Purification of 7,7',8,8'-tetrachloro-3,3',3',3'-tetramethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[cyclopenta[b]phenazine] (tetrachloro monomer) (Figure 2.14).

![Figure 2.14 The structure of the tetrachloro monomer.](image)

The crude tetrachloro monomer (4.69 g) was recrystallised from toluene (250 cm$^3$). The recrystallisation was performed twice and the product dried to give 2.39 g (43.27%) yield. $^1$H-NMR characterisation gave $\delta$H 1.7 (12 H, br, CH$_3$), 2.7 (4 H, br, CH$_2$), 7.3 - 8.5 (8 H, br, aromatic). Elemental analysis data was C, 63.65 %, H, 3.84 %, N, 8.53 %, and Cl, 22.07 %. C$_{33}$H$_{24}$N$_4$Cl$_4$ was expected to give C, 64 %, H, 3.9 %, N 9.1 %, Cl, 23 %.

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Sorption of Gases and Liquids by Polymers of Intrinsic Microporosity (PIMs)
Stage 5: Polymerisation of tetrachloro monomer and 5,5’,6,6’-Tetrahydroxy-3,3,3’,3’-tetramethyl-1,1’-sporobisindane-A (Figure 2.15).

![Polymerisation of tetrachloro monomer and 5,5’,6,6’-Tetrahydroxy-3,3,3’,3’-tetramethyl-1,1’-sporobisindane](image)

**Figure 2.15: Polymerisation of tetrachloro monomer and 5,5’,6,6’-Tetrahydroxy-3,3,3’,3’-tetramethyl-1,1’-sporobisindane**

Tetrachloro monomer (2.39 g, 3.86 mmol), 5,5’,6,6’-Tetrahydroxy-3,3,3’,3’-tetramethyl-1,1’-sporobisindane (1.31 g, 3.86 mmol), 18-crown-6 (1.02 g, 3.86 mmol) and DMF (60 cm³) were refluxed at 150 °C under dry N₂ with stirring. After allowing the monomers to equilibrate to temperature, K₂CO₃ (4.26 g, 30.87 mmol) was added and refluxed for 48 hours at 150 °C. After allowing the reaction mixture to cool down to room temperature, it was added to deionised water (1 000 cm³) and stirred for 1 hour. The product was collected by vacuum filtration and washed with deionised water and methanol. The yield of the unpurified product was 2.99 g (91.55%).

The crude PIM-7 was purified by precipitation into a non-solvent to remove oligomers and low molecular weight product. A solution of PIM-7 (2.99 g) in chloroform (120 cm³) was prepared, filtered through glass wool and added drop-wise to a vigorously stirred THF solution and stirred for an hour. This precipitation step was performed twice. The product was collected by vacuum filtration, washed with THF and dried in a vacuum oven at 100 °C. ¹HNMR characterisation (400 MHz, CDCl₃) gave δH 1.70 (24 H, br, m), 2.70 (8H, br, m), 7.30, 8.10, 8.30, and 8.50 (12 H, br, aromatic). Elemental analysis gave C, 77.9 %, H, 5.5 %, and N, 6.9 % (The molecular formula of C₅₄H₄₄O₄N₄ requires C, 79.8 %, H 5.46 %, N 6.8 %, O 7.94 %).
2.4.5 Polymer film preparation

2.4.5.1 Thin films – spin-coating

A polymer solution was prepared by dissolving PIM-1 (0.1869 g, 0.41 mmol) in chloroform (9.3 ml) and stirring overnight at room temperature. The solution was then filtered through glass wool and spin-coated onto silica substrate using a Laurell WS-400B-6NPP/LITE spin-coater (1 000 rpm for 120 s). Use was made of a Dektak 8 Programmable Surface Profiler Measuring System set at scan length 250 -1000 Å, and a scan time of 1 min, to measure the film thickness, $t$ after scratching off a thin line of polymer coating layer with a hypodermic needle. After drying in air for at least a week, the films were carefully peeled off and placed in enough methanol to immerse them. These were left for at least 10 h at room temperature before drying them in a vacuum oven for at least 8 h. After this treatment they were ready for sorption analysis using the ASAP 2020 volumetric analyser.

2.4.5.2 Thick films – solvent evaporation

Thick dense polymer films were prepared by solvent evaporation of a 1.5 wt % solution of PIM-1 in chloroform, cast on a glass petri dish. This was placed in a closed desicator with a constant purge of N₂ gas for three days to evaporate the solvent. To remove residual solvent, the films were vacuum dried at 120 °C for at least 8 hours. Measurements of membrane thickness were taken using a Deltascope MP30 equipped with an ED10 probe and the results averaged. The average was compared to the theoretical value calculated using the mass of the polymer, $m$, its density, $\rho$, and the resulting film area, $A$ as shown in Equation 2.10.

$$ t = \frac{m}{\rho A} \quad (2.10) $$
2.4.6 Characterisation Techniques

2.4.6.1 Elemental Analysis

About 6 mg of solid sample was weighed into a sample vial and submitted to the School of Chemistry, University of Manchester, using a Carlo Erba 1108 Elemental Analyser for the percentage of Carbon, Hydrogen and Nitrogen.

2.4.6.2 Nuclear Magnetic Resonance (¹HNMR) Spectroscopy

The samples were prepared by dissolution of a few milligrams of polymer in CDCl₃ and filtered through glass wool. A Bruker 400 MHz spectrometer was used to obtain ¹HNMR spectra. The resulting chemical shifts were reported as parts per million (δ) using tetramethylsilane (TMS) as an internal standard.

2.4.6.3 Matrix Assisted Laser Desorption / Ionization Time of Flight (MALDI ToF) Mass Spectrometry

About 4 mg of solid sample of polymers was weighed into a sample vial and submitted for MALDI ToF analysis. The spectra were recorded on a Micromass ToF Spec 2e spectrometer equipped with a nitrogen laser at 337 nm. The matrix used was Dithranol with sodium bromide as the dopant. The solvent used was tetrahydrofuran (THF).

2.4.6.4 Attenuated Total Reflection Fourier transform Infrared Spectroscopy (ATR-FT-IR) measurements

FT-IR spectra were recorded on a FTS 6000 Biorad spectrometer equipped with an ATR setup, and annexed to a Whatman FTIR purge gas generator. The spectra were recorded in the attenuated total reflection (ATR) mode, with a resolution of 0.25 cm⁻¹, a sensitivity of 1, and 20 scans in the range 4000 – 600 cm⁻¹ were averaged for each spectrum.

2.4.6.5 Gel Permeation Chromatography (GPC)

0.2 % w/v solutions of polymer samples were prepared in chloroform and filtered through a 0.45 μm syringe microfilter (Gelman Science). The flow rate was kept at 1 ml per minute. The injection volume used was 100 μL. The GPC experiments were performed on a Multiple detector GPC using a Viscotek GPCmax
VE2001 instrument, with three 30 cm Polymer Labs PLgel columns (2 x 10 $\mu$m MIXED-B and 1 x 10 $\mu$m 500 Å) along with a Viscotek TDA 302 triple detector array that combines the refractive index, intrinsic viscosity, and light scattering detectors.

2.4.6.6 BET Surface Area measurements

(a) Sample preparation

The material under study was finely ground in a mortar and pestle before being transferred into a sample vial and placed into the drying chamber of a vacuum oven. The sample vial was covered by a perforated aluminium foil to avoid the sample being sucked out of the vial by the sudden application of the vacuum. The vacuum oven temperature was set to 120 °C and maintained at that for at least 4 hours after which it was cooled to room temperature under vacuum. At the end of the heating and cooling cycle the sample vial was removed and sealed. The sample tube was placed into the vacuum oven and dried for at least 1 hour to remove any adsorbed material. After being cooled to room temperature it was quickly sealed by an air tight rubber bung. It was then purged with dry N$_2$ gas before being sealed again and weighed to 4 decimal places. About 100 mg of the dried sample was weighed into the sample tube, ready for transfer onto the porosimeter (ASAP 2020 or Coulter 3100).

(b) Analysis

Nitrogen and carbon dioxide adsorption/desorption studies were undertaken using the Micromeritics ASAP 2020 surface area and porosimetry analyser (Norcross, GA). To remove residual adsorbed materials from the surface, the samples were first heated in a sample tube under vacuum and kept at that pressure and temperature for a set length of time. After that the sample tube was attached to the analysis port and an evacuation performed at ultrahigh vacuum (10$^{-9}$ bar). This done, the sample was then put under the analysis programme where it was inundated with high purity research grade gas of minimum purity 99.99 % supplied by BOC Gases Ltd, and adsorption data collected. Free space determination was performed at the end of the analysis using helium (99.9999% purity) at ambient temperature and 77 K. Using multi-point BET analysis (Chapter 1) apparent surface areas were calculated from N$_2$ adsorption data. Details of how the sorption methodology was validated are described in Chapter 3.
(c) Free space Measurement

In order to ascertain the density of the materials under test, warm and cold free spaces are measured after analysis. Warm free space was determined by measuring the sample tube gas capacity at room temperature, whereas the cold free space is the sample tube gas capacity measured when the liquid nitrogen dewar is elevated, ie. at 77 K. Free space measurement is done at the end of the analysis to avoid the material under test from retaining the helium gas used for the measurement, which may alter the adsorptive properties.

Using appropriate mathematical formulae, the measured free spaces thus obtained can be used to estimate sample densities.

\[
V_{ws} = V_{wm} - \left( \frac{M_s}{\rho_s} \times \frac{T_{std}}{T_{amb}} \right) \tag{2.18}
\]

\[
V_{cs} = V_{cm} - \left( \frac{M_s}{\rho_s} \times \frac{T_{std}}{T_{bath}} \right) \tag{2.19}
\]

Where \( V_{ws} \) (cm\(^3\)) is calculated warm free space with sample present in standard, \( V_{wm} \) (cm\(^3\)) is warm free space measured for empty tube in standard, \( M_s \) (g) is the mass of the sample, \( \rho_s \) (g cm\(^{-3}\)) is the approximate sample density, \( T_{amb} \) (K) is the ambient temperature (298 K), and \( T_{std} \) (K) is the standard temperature (273 K).

\( V_{cs} \) (cm\(^3\)) is the calculated cold free space with sample present in standard, \( V_{cm} \) (cm\(^3\)) is the cold free space measured for empty tube in standard, \( T_{bath} \) (K) is the analysis bath temperature.
2.5 Results and Discussion

2.5.1 N₂ (77 K) adsorption isotherms

2.5.1.1 PIM-1, PIM-2, PIM-7 and TAPIM-1

A comparison of the N₂ (77 K) sorption isotherms for PIM-1, PIM-2, PIM-7 and TAPIM-1 is shown in Figure 2.16. The N₂ isotherms are characteristic for microporous materials. The low relative pressure region shows significantly high adsorption for PIM-1 than the other three. Hence PIM-1 has the highest surface area, followed by PIM-7, then PIM-2, and TAPIM-1 has the lowest (Table 2.2).

As expected for microporous materials, the N₂ adsorption at low relative pressures for both PIM-7 and TAPIM-1 is significantly high. PIM-1, PIM-2 and PIM-7 each adsorb a higher quantity of gas than the thioamide before the isotherm reaches the knee. The BET surface area of the thioamide (420 m² g⁻¹) is consequently lower than for the other three as shown in Table 2.2.
2.5.1.2 Triptycene based PIMs (TripPIMs)

The N$_2$ (77 K) sorption isotherms for the triptycene family are shown in Figure 2.17. The low pressure regions of the isotherms show high N$_2$ adsorption characteristic of microporous materials. These materials adsorb more gas and are consequently more porous than PIM-1, PIM-2, PIM-7 and TAPIM-1.

![Figure 2.17 N$_2$ (77 K) sorption isotherms for BD107 (adsorption: black dots, desorption: black circles), BD34 (green triangles), BS14 (black triangles), BS138 (blue diamonds), BS13 (purple dots), and BS30 (red triangles). Bold symbols represent adsorption, and blank symbols represent desorption.](image)

The BET surface areas for the triptycene based PIMs are shown in Table 2.3. Triptycene based PIMs are network polymers that cannot dissolve in THF or chloroform, and hence cannot be cast into films.
2.5.1.3 PIM-1 Ethano-anthracene copolymers

The nitrogen adsorption/desorption isotherms of PIM-1 copolymers are shown in Figure 2.18. PIM1-CO1-100 is a homopolymer, PIM1-CO1-61 has 39% spiro-unit content, and so forth. \( \text{N}_2 \) sorption measurements show that these co-polymers adsorb comparable amounts of nitrogen to that of PIM-1. Surface area determination using nitrogen adsorption measurements (using \( \text{N}_2 \) and multi-point BET calculation) show that the co-polymer materials have high surface areas in the range 700–800 m\(^2\)g\(^{-1}\) (Table 2.3) with very significant adsorption at low relative pressure (\( p/p^0 < 0.01 \)) indicating microporosity.\(^{15, 37} \) Interestingly, the maximum capacity for adsorption (at \( p/p^0 = 1 \)) decreases in the order CO1-50>CO1-40>CO1-61>CO1-100, whereas in the low relative pressure region (\( p/p^0 < 0.3 \)), the trend is CO1-40>CO1-50>CO1-61>CO1-100. There is distinctly less hysteresis at higher PIM-1 levels. BET surface area decreases in the order CO1-50>CO1-40>CO1-100>CO1-61. The enhanced adsorption at high relative pressure is associated with large hysteresis, which is probably due to the swelling of the polymer network.

![Figure 2.18 N\(_2\) (77 K) adsorption for PIM-1 co-polymers. PIM1-CO1-40 (blue diamonds), PIM1-CO1-50 (black squares), PIM1-CO1-61 (green dots), and PIM1-CO1-100 (red triangles). Adsorption is shown by bold plots and desorption by blank ones.](image-url)
2.5.1.4 3,3',4,4'-tetra(trimethylsilylethynyl)biphenyl (organic crystal)

As shown in Figure 2.19, there is a very significant level of nitrogen adsorption at 77 K, particularly at low relative pressures (3.3 mmol at $p/p^0 = 0.1$). This is commensurate with a microporous material. Following the general classification of adsorption isotherms the general shape of the adsorption isotherm appears to be a simple Type I isotherm. From the data, a BET surface area of about 280 m$^2$ g$^{-1}$ and a micropore volume of 0.16 ml g$^{-1}$ can be calculated. The total amount of nitrogen adsorption of 4.4 mmol g$^{-1}$ at $p/p^0 = 1$ is quite significant, considering this is a crystalline material composed of a low molar mass organic compound.

Figure 2.19 N$_2$ (77 K) adsorption (bold diamonds) and desorption (blank diamonds) isotherms for 3,3',4,4'-tetra(trimethylsilylethynyl)biphenyl.
2.5.2 Summary

A summary of the characterisation data for the materials synthesised at Manchester is presented in Table 2.2.

### Table 2.2 Characterisation data for materials synthesised at Manchester

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>BET surface area (m² g⁻¹)</th>
<th>Weight average molecular mass, ( M_w ) (D)</th>
<th>Number average molecular mass, ( M_n ) (D)</th>
<th>Polydispersity ( (M_w/M_n) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>JDS057</td>
<td>750</td>
<td>97 000</td>
<td>39 000</td>
<td>2.49</td>
</tr>
<tr>
<td>CT/02/07</td>
<td>790</td>
<td>158 000</td>
<td>55 000</td>
<td>2.87</td>
</tr>
<tr>
<td>PBCM35</td>
<td>420</td>
<td>Insoluble</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CZ11</td>
<td>530</td>
<td>19 000</td>
<td>4 500</td>
<td>4.2</td>
</tr>
<tr>
<td>CZ3</td>
<td>720</td>
<td>78 000</td>
<td>28 000</td>
<td>2.79</td>
</tr>
</tbody>
</table>

PIM-1 samples (JDS057 and CT/02/07) have the highest BET surface area and average molar mass. TAPIM-1 (PBCM35) formed an insoluble orange lump, which turned bright orange with time. Its solubility in DMSO also decreased with time. This could be due to network formation with time. This gradual networking could be responsible for the low BET surface area compared to the other PIMs. The BET surface area was also found to decrease with time.

Table 2.3 shows BET surface area data for materials sourced from elsewhere.
Table 2.3 BET surface area data for materials sourced from elsewhere

<table>
<thead>
<tr>
<th>Sample code</th>
<th>BET surface area (m² g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Triptycene based PIMs</strong></td>
<td></td>
</tr>
<tr>
<td>KJM103</td>
<td>1318</td>
</tr>
<tr>
<td>BD107</td>
<td>1730</td>
</tr>
<tr>
<td>BS14</td>
<td>1343</td>
</tr>
<tr>
<td>BD34</td>
<td>1417</td>
</tr>
<tr>
<td>BS138</td>
<td>978</td>
</tr>
<tr>
<td>BS13</td>
<td>947</td>
</tr>
<tr>
<td>BS30</td>
<td>618</td>
</tr>
<tr>
<td><strong>PIM-1 ethano-anthracene copolymers</strong></td>
<td></td>
</tr>
<tr>
<td>KH39</td>
<td>760</td>
</tr>
<tr>
<td>KH40</td>
<td>790</td>
</tr>
<tr>
<td>KH37</td>
<td>720</td>
</tr>
<tr>
<td>KH50</td>
<td>750</td>
</tr>
<tr>
<td><strong>3,3′,4,4′-tetra(trimethylsilylethynyl)biphenyl</strong></td>
<td></td>
</tr>
<tr>
<td>KJM30R5</td>
<td>280</td>
</tr>
</tbody>
</table>

A discussion of the BET surface areas of triptycenes is provided in section 3.4.5.4.

2.5.3 Film-forming ability

Except for TAPIM-1, the materials synthesised at Manchester are non-network PIMs, as a result they can be dissolved in a solvent (THF or chloroform) and cast into membranes or films. The film-forming ability of the materials synthesised at Manchester are shown in Table 2.4. Film-forming ability has been known to depend, among other factors, on the molecular weight of the polymer.

Table 2.4 Film-forming ability

<table>
<thead>
<tr>
<th>Sample</th>
<th>Film</th>
</tr>
</thead>
<tbody>
<tr>
<td>JDS057</td>
<td>Flexible, free standing film</td>
</tr>
<tr>
<td>CT/02/07</td>
<td>Flexible, free standing film</td>
</tr>
<tr>
<td>CZ3</td>
<td>Brittle film</td>
</tr>
<tr>
<td>CZ11</td>
<td>Brittle film</td>
</tr>
</tbody>
</table>
Both PIM-1 batches (JDS057 and CT/02/07) are readily soluble in chloroform and form flexible, free standing films. PIM-2 and PIM-7 form brittle films which can only be characterised when spin-coated onto a suitable substrate like glass or silica wafers. Because TAPIM-1 (PBCM35) was insoluble in neither THF nor chloroform, it was not possible to cast it into a film. The reason for its insolubility could be that it forms networks through hydrogen bonding. This is explored further in Chapter 3.
2.6 Conclusion

The following conclusions can be made.

Spectroscopic data for all the materials show the presence of the expected functional groups for each of the materials synthesised indicating that the respective syntheses were successful.

PIM-1 can be fabricated into self-standing membranes that can be used for other applications. However, PIM-2 and PIM-7 can only form brittle membranes but should be blendable with proportions of PIM-1 to give reasonably self-standing membranes. The applications of such membrane blends are yet to be explored. Even when materials cannot form self-standing robust membranes, they can be spin-coated onto suitable substrates like glass or silica on which measurements and further investigations can be performed.

The BET surface areas of all the PIMs synthesised show they are highly porous materials. Overall, the BET surface areas of all the PIMs are much higher than other organic polymers. The isotherms are typical type II (BET) isotherms indicating unrestricted monolayer-multilayer adsorption. It should be interesting therefore, to study the distribution of the micropores in each of these materials. Chapter 3 will look at the use of various models, especially the Horvath-Kawazoe model, in characterising pore size distributions in the materials discussed in this chapter.

Triptycene based PIMs are highly microporous materials with high BET surface areas. They owe their enhanced microporosity to their macromolecular shape of the framework which reduces rotation and frustrates efficient packing. Because they form networks, they cannot be dissolved and cast into films.
Chapter 3: Gas Sorption Studies
Chapter 3: Gas Sorption Studies

3.1 Introduction

In this chapter, the theoretical approaches of a number of sorption models are discussed. Thereafter, different approaches to obtaining pore size distribution (PSD) data are dealt with. Attention is paid to gas sorption methods that use CO\(_2\), N\(_2\), H\(_2\), and other gases to determine PSD. The Horvath-Kawazoe model is presented as the preferred model and the N\(_2\), CO\(_2\) and H\(_2\) sorption data are treated under this approach. A brief discussion is presented on the validation of both the sorption methodology, which is validated using standard reference materials (SRMs), and the PSD evaluation, using a well defined crystalline material. CO\(_2\) PSD data at 273 K and at 303 K is compared against N\(_2\) PSD data and a complementary relationship established. The influence of polymer form (powder or film) and structure is investigated using PIM-1 and PIM-2, PIM-1 ethano-anthracene copolymers, and triptycene based PIMs.

3.1.1 Physical Adsorption

The physical adsorption of a gas is closely related to the condensation of a vapour and, for N\(_2\), occurs to an appreciable extent only below the critical temperature. This is an easily reversible process and is not accompanied by significant changes in the chemical properties of the system. Adsorption is a surface phenomenon, and so the quantity of gas taken onto the surface is usually small except when the solid has high surface area. This is why highly porous materials like silica gel and charcoals are used as adsorbents.

The adsorption isotherm is a key property of an adsorbate-adsorbent system. It consists of an equation or model that represents the relationship between the amount of adsorbate adsorbed by unit mass of adsorbent at constant temperature, and the pressure of the adsorbate. Models of gas adsorption enable quantitative comparisons between the porosity properties of different porous materials.
3.1.2 Empirical isotherms

The quantity of gas molecules, \( n \), taken up by mass, \( m \), of a surface depends on several variables including temperature, \( T \), pressure, \( p \), surface energy distribution, and the surface area and porosity of the solid. The mathematical relation can be written as in Equation 3.1.

\[
\frac{n}{m} = f(p, T, \text{system})
\]  

(3.1)

At constant temperature this gives Equation 3.2:

\[
\frac{n}{m} = f(p)_T
\]  

(3.2)

Below \( T_{\text{critical}} \), this becomes Equation 3.3:

\[
\frac{n}{m} = f\left(\frac{p}{p^0}\right)_T
\]  

(3.3)

Where \( p^0 \) is the saturation pressure of the adsorptive at temperature \( T \).

The above expression represents the adsorption isotherm,\(^{19}\) which is basically a measure of the molar quantity of gas adsorbed at constant temperature by an initially clean solid surface as a function of gas pressure. Adsorption isotherms reveal a great deal about the structure of the adsorbing material simply from their shape/form.\(^{78}\) The form of the isotherm is influenced by the micropore distribution in that a higher concentration of ultramicropores (pore size <0.7 nm), as found in PIMs, is associated with enhanced low pressure adsorption.\(^{29}\)

Many different types of isotherms have been reported in the literature.\(^{77, 79, 80}\) These isotherms can have different shapes depending on the intermolecular interactions between the adsorbent and adsorbate. Brunauer, Deming, Deming and Teller (BDDT)\(^{81}\) were the first to systematically classify isotherms in the 1940s. They grouped them into five categories on which the IUPAC system is
based. These isotherms, together with a sixth one introduced by Sing, are illustrated in Figure 3.1.

![Figure 3.1: An illustration of the IUPAC classification of isotherms](image)

3.1.2.1 Type I isotherms

The type I isotherm is concave to the $p/p_0$ axis. It corresponds to the Langmuir isotherm. It characterises microporous adsorbents. The plateau of a well defined type I isotherm covers a broad range of $p/p_0$ and its gentle gradient shows little multi-layer adsorption.

3.1.2.2 Type II isotherms

The type II isotherm is concave to the $p/p_0$ axis, then almost linear before being convex to the $p/p_0$ axis. This is the most common type of isotherm. It describes adsorption on microporous adsorbents with strong adsorbate-adsorbent interactions. The BET multi-layer adsorption theory was originally developed for this type of isotherm. This type of isotherm is therefore characteristic of multi-layer adsorption, indicating the presence of non-porous or macroporous surfaces.
3.1.2.3 Type III isotherms

This type of isotherm is convex to the \( p/p^0 \) axis. It describes adsorption on macroporous adsorbents with weak adsorbate-adsorbent interactions.

3.1.2.4 Type IV isotherms

The initial region of the type IV isotherm is related to the type II isotherm. Type IV isotherms represent adsorption isotherms with hysteresis. This type of isotherm gives useful information on the mesopore structure. In mesopores, molecules form a liquid-like adsorbed phase with a meniscus whose curvature is described by the Kelvin equation, and this gives a pore size distribution.

3.1.2.5 Type V isotherms

This type is initially convex to the \( p/p^0 \) axis and levels off at high \( p/p^0 \). Closely similar to type IV, type V isotherms represent isotherms with hysteresis.

3.1.2.6 Type VI isotherms

This isotherm is stepped. The steps arise from phase transition of the adsorbed molecular layer or adsorption on the different faces of crystalline solids.

The BDDT and IUPAC classification of isotherms is incomplete and it gives the impression that the quantity adsorbed always varies monotonically with pressure. Nevertheless, analyses of physical adsorption isotherm data gives vast information on the total surface area, mesopore and micropore volume and area, total pore volume, the distribution of pore volume and area by pore size, and surface energy distribution.\(^{78}\)

Information about pore size can be obtained from the shape of the adsorption isotherm. For example, when the adsorbent is predominantly microporous, a type I isotherm results, whereas a type IV isotherm indicates mesoporosity. Detailed information on microporosity can be obtained by plotting the isotherm on a logarithmic \( p/p^0 \) scale. The logarithm of \( p/p^0 \) represents the free energy upon adsorption, \( \Delta G = RT \ln(p/p^0) \).\(^{83-85}\) Kinks or peaks on the graph show the filling of different pore sizes. If this does not readily show a discernible trend, a plot of
\[
dQ / \ d \log(p/p^0) \text{ against } \log(p/p^0) \text{ should show more clearly where the turning points and the inflection points are on the isotherm. } Q \text{ is the quantity of gas adsorbed. Since for each } p/p^0 \text{ value there is a corresponding pore width, this is similar to plotting } dQ/dw \text{ against } w, \text{ the pore width.}^{33}
\]

### 3.1.3 Sorption models

#### 3.1.3.1 The Langmuir model

During the early 20th century, Langmuir put forward a simple model of adsorption,\(^{32}\) the Langmuir Isotherm. This assumes monolayer coverage. The other key assumptions are:

i. The surface contains \(N\) independent and equivalent sites each of which may be occupied by a single molecule,

ii. There is a dynamic equilibrium between the gas and the adsorbed layer,

iii. An adsorbing molecule will stick upon striking a vacant site, if this site is occupied it gets reflected back to the bulk, and

iv. Once adsorbed molecules are localised there is no migration.

If the rate of adsorption is proportional to the product of the fraction of uncovered surface and gas pressure, and if the desorption rate is directly proportional to the fraction of the surface already covered by gas molecules, then it is possible to arrive at the Langmuir isotherm (Equation 3.4).

\[
k_a p (1 - \theta) = k_d \theta
\]

This basically says at equilibrium the rates of adsorption and desorption are equal. The constants \(k_a\) and \(k_d\) are adsorption and desorption constants respectively, and \(\theta\) is the fraction of surface covered by gas molecules at equilibrium. By making \(a = k_d/k_a\) and rearrangement, Equation 3.4 becomes Equation 3.5.

\[
\theta = \frac{p}{a + p}
\]

Assuming there is no attraction between adsorbent and adsorbate at distances greater than one molecular diameter, the adsorbed layer thickness cannot exceed
one molecular diameter. Consequently, the quantity of adsorbed gas is proportional to $\theta$ so that (introducing another constant $x_m$)

$$x = \frac{x_m p}{a + p}$$  \hspace{1cm} (3.6)

Equation 3.6 is the Langmuir isotherm, which yield isotherms similar to Type II. From this equation, as $p \to \infty$ (complete monolayer coverage of surface), $x = x_m$. Knowing $x_m$ allows the calculation of the surface area of the adsorbent. Decomposing Equation 3.6 into a linear form (Equation 3.7) allows $a$ and $x_m$ to be determined from the intercept and gradient of the plot of $p/x$ against $p$.

$$\frac{p}{x} = \frac{p}{x_m} + \frac{a}{x_m}$$  \hspace{1cm} (3.7)
3.1.3.2 Dual mode approach

The dual mode sorption model has been used to explain the reduction in permeability of a glassy polymer membrane with increasing feed pressure.\(^{26, 86, 87}\)

![Diagram showing the Dual Mode Sorption Model](image)

**Figure 3.2** The Dual Mode Sorption Model showing that the total amount of gas adsorbed is a superposition of Henry mode and Langmuir mode sorption.\(^{88}\)

The total quantity of gas adsorbed at any given pressure is the sum total of Henry’s mode and the Langmuir mode (Figure 3.2). Thus it combines the two independent processes of Henry solution, as observed in liquids or rubbery polymers, with the Langmuir adsorption process on inner surfaces of microporous materials. There are therefore two different adsorption sites, the Henry type and the Langmuir type adsorption sites. Consequently, there are two populations of adsorbed gas molecules. The underlying assumption here is that the polymer under investigation is glassy, and matrix deformations owing to plasticisation are insignificant. This is the Dual Mode sorption model.

Henry’s law\(^{38, 88}\) relates the adsorptive concentration to the pressure linearly as shown in Equation 3.8:

\[
C_D(p) = k_D p \tag{3.8}
\]
Where $k_D$ is the solubility coefficient of the gas in the polymer. This is represented by the straight line in Figure 3.2. The Langmuir isotherm, $C_H$, describes the pore filling of micropores with a saturation capacity $C'_H$ and the affinity constant $b$ as follows:

$$C_H(p) = \frac{C'_H b p}{1 + b p} \quad (3.9)$$

Thus the pressure dependent concentration $C(p)$ is given by the sum of Henry mode and the Langmuir mode:\[38, 86, 87, 89\]

$$C(p) = C_D + C_H = k_D p + \frac{C'_H b p}{1 + b p} \quad (3.10)$$

This is the bold line in Figure 3.2. Henry’s law behaviour, $C_D$ was originally assumed to be associated with the dense regions of the polymer, and Langmuir behaviour, $C_H$ was originally assumed to be associated with holes or microvoids within the polymer. At low pressure, adsorption follows the Langmuir mode, and at higher pressures it reaches a constant gradient where the Henry mode becomes more dominant. Whereas the Langmuir model can be used to describe a pore-filling mechanism, the Henry adsorption describes pore dilation which results in swelling of the polymer. This swelling, $\Delta V$, is related to the original polymer volume, $V_0$, by Equation 3.11:\[88\]

$$\frac{\Delta V}{V_0} = \frac{V_p}{V_{id}} C_D = \frac{V_p}{V_{id}} k_D p \quad (3.11)$$

where $V_p$ is the partial molar volume of the adsorptive gas, and $V_{id}$ is the volume of ideal gas at standard temperature and pressure (STP). Thus, to account for both the Langmuir and Henry modes on an isotherm, the following relation is used:

$$\frac{\Delta V}{V_0} = \frac{V_p}{V_{id}} C_D + f \frac{V_p}{V_{id}} C_H = \frac{V_p}{V_{id}} \left[ k_D p + f \left( \frac{C'_H b p}{1 + b p} \right) \right] \quad (3.12)$$

Clearly, the two populations of sorbed gas molecules exhibit different partial molar volumes.
Sorption of Gases and Liquids by Polymers of Intrinsic Microporosity (PIMs)

3.1.3.3 BET model

The adsorption isotherm is caused simultaneously both by physical multilayer adsorption and capillary condensation. According to the Langmuir theory, adsorption is assumed to occur as a monolayer. This assumption has since been refuted because it only explains adsorption isotherms partly. The commonly used model for determining surface area is the BET (Brunauer, Emmett, Teller) model, which basically extends the Langmuir theory to multilayer adsorption and generates a type II isotherm (Figure 3.1). This is a theory that assumes that adsorption occurs as multilayers so that the penultimate layers may start forming even before full coverage of the surface (Figure 3.3). The adsorbed molecules in one layer can also act as adsorption sites for molecules in the next layer. The forces active in the condensation of gases are also responsible for the binding energy in multimolecular adsorption.\(^{19}\)

![BET adsorption model showing layers of gas molecules adsorbed onto a surface.](image)

Taking \(s_i\) to represent the part of adsorbent surface that is covered by \(i\) adsorbed molecule layers, the uncovered surface \(s_0\), must be constant at equilibrium. The condensation on the uncovered surface should equal the evaporation from the first layer. Using the kinetic theory of gases to evaluate condensation, and the heat of adsorption to calculate evaporation, this gives (at equilibrium):

\[
a_i p s_0 = b_i s_i e^{-E_i/RT} \quad (3.13)
\]

where

\(p\) is pressure
$E_1$ is the modulus of the energy of adsorption of the first layer.

$R$ is the universal gas constant.

$T$ is absolute temperature.

$a_1, b_1$ are adsorption and desorption constants for the first layer.

The left hand side of the equation represents condensation, and the right hand side represents evaporation. At equilibrium the area of the surface covered by one molecular layer, $s_1$ is constant. It can however, be altered in four different ways, namely by condensation on the uncovered surface, through evaporation from the first layer, by condensation on the first layer or, by evaporation from the second layer. Thus,

$$a_2 p s_1 + b_1 s_1 e^{-E_1/RT} = b_2 s_2 e^{-E_2/RT} + a_1 p s_0$$

(3.14)

where

$E_2$ is the heat of adsorption of the second layer, and

$a_2, b_2$ are adsorption and desorption constants for the second layer.

Combining Equations 3.13 and 3.14 yields:

$$a_2 p s_1 = b_2 s_2 e^{-E_2/RT}$$

(3.15)

Using the same argument gives for the $i^{th}$ layer:

$$a_i p s_{i-1} = b_i s_i e^{-E_i/RT}$$

(3.16)

The total surface area of the adsorbent is:

$$A = \sum_{i=0}^{\infty} s_i$$

(3.17)

and the volume adsorbed is:

$$V = v_0 \sum_{i=0}^{\infty} i s_i$$

(3.18)
where $v$ is the volume adsorbed, and $v_0$ is the volume of a complete monolayer per square centimetre.

Rearranging 3.17 and combining with 3.18 gives:

$$\frac{v}{A v_0} = \frac{v}{v_m} = \sum_{i=0}^{\infty} \frac{i S_i}{s_i}$$

(3.19)

where $v_m$ is the volume of a complete monolayer covering surface $A$.

Assuming the heat of adsorption is constant and equal to $E_L$, and excluding the heat of adsorption of the first layer, assuming the ratio of the constants $b_i$ and $a_i$ is constant (at constant temperature) equal to $g$, and taking $x = (p/g)e^{E_L/RT}$, and $c = (a_i g / b_i)e^{(E_i - E_L)/RT}$ yields:

$$\frac{v}{v_m} = \frac{c S_0}{s_0} \sum_{i=0}^{\infty} \frac{i x^i}{1 + c \sum_{i=0}^{\infty} x^i}$$

(3.20)

lim $p \to p^0$, $v \to \infty$. Thus $x = 1$ at $p = p^0$. Equation 3.20 therefore becomes:

$$\frac{v}{v_m} = \frac{c \left( \frac{p}{p^0} \right)}{\left( 1 - \frac{p}{p^0} \right) \left( 1 - \frac{p}{p^0} + c \frac{p}{p^0} \right)}$$

(3.21)

Rearranging 3.21 gives:

$$\frac{p}{v(p^0 - p)} = \frac{1}{v_m C} + \frac{(C-1)(p/p^0)}{v_m C}$$

(3.22)

$C$ is a constant.
From this equation a plot of $\frac{p}{V_0}(p^0 - p)$ against $\frac{p}{p^0}$ is linear with intercept $\frac{1}{V_m C}$ and gradient $(C - 1)\frac{1}{V_m C}$. This will allow the determination of the values of $V_m$ and $C$. Isotherm data for most solid materials when using nitrogen as the adsorptive will yield a straight line in the range $0.05 < \frac{p}{p^0} < 0.3$. Using the area occupied by a single molecule, the surface area, $A$, of the material can be obtained from Equation 3.23.

$$A = \left(\frac{V_m}{22414}\right) \times \sigma \times N_A$$

(3.23)

where $N_A$ is Avogadro’s number, and $\sigma$ is the area of surface occupied by a single adsorbed gas molecule.
3.1.4 Pore size Distribution (PSD)

Pore size distribution (PSD) is the distribution of pore volume with respect to pore size. Among the properties that are considered in the manufacture of adsorbents and porous materials in general for particular applications, pore size distribution and the pore volume are important parameters. The pore size distribution determines the pore volume accessible to molecules of a certain size. Whereas the synthesis of microporous materials has met with significant success, porosity determination is lagging behind.4

It has been demonstrated that a predominance of ultra-micropores (0.6 – 0.8 nm) maximises hydrogen storage capacity.93, 94 Micropores play an important role in the design of materials for adsorption, catalysis, molecular sieving processes85,4, 95 and gas separation in membrane applications.96, 97 Thus PSD determination is an important physicochemical parameter.

3.1.4.1 Gas sorption

Gas adsorption studies, especially N2 sorption at 77 K, are routinely used to characterise porous materials. Nitrogen and carbon dioxide adsorption have been found to provide an indication of hydrogen storage capacity. These gaseous probes have subsequently been used to establish an appropriate methodology for characterising micropore distributions.98 Micropores of certain sizes (ultramicropores) are expected to exhibit strong H2 uptake. The advantage of using the N2 probe is that it can cover relative pressures from 10-8 to 1 bar, thus generating adsorption data in a broader range of porosity. Consequently, CO2 as a complementary technique for N2 adsorption will be reported in this document and extrapolated to H2 adsorption capacities. In addition, CO2 sorption studies are also of interest because they give information on the capacity of materials to be used in carbon capture applications. Despite being a very useful probe, N2 can cause swelling to soft polymeric materials. This results in a hysteresis loop within the low pressure region.4 Because for some materials a N2 isotherm takes very long to acquire, the resulting isotherm might not be representative of the equilibrium state. This will consequently have a bearing on the PSD obtained from this data. In addition, some pores are not accessible to the N2 probe, thus use is made of complementary techniques like the use of CO2 or other independent techniques like PALS or 129Xe NMR to probe the free volume.
The evaluation typically involves the acquisition of a gas adsorption isotherm using a selected adsorptive (e.g. \(\text{N}_2\), \(\text{CO}_2\) or \(\text{Ar}\)), followed by analysis and the transformation of the isotherm data into structural information using mathematical operations that constitute a model. The resulting output is known to be model dependent.\(^4\)

A direct experimental technique involves measuring the saturated quantities of adsorbed probe molecules of differing sizes and geometries. This technique however, is time-consuming and has inherent errors owing to networking effects so that some pores remain unprobed.\(^99\). PSD can also be calculated from a single adsorption isotherm\(^99, 100\) (Equation 3.24) where the amount adsorbed is equated to the integral of the product of the quantity adsorbed in a specific pore size and the PSD over all sizes.

\[
W(p) = \int_\theta^\infty w(L, P) f(L) dL
\]

(Equation 3.24)

where \(w(L, P)\) is the amount of gas adsorbed in pores size \(L\), and \(f(L)\) is the PSD function. Despite being experimentally convenient, this method is limited by the assumptions it makes.

### 3.1.4.2 Pore size and Pore Geometry

Supposing all pores were of spherical geometry, their size would be defined explicitly by their diameter or radius. If cylindrical, the length along one edge would be characteristic; if of some other regular shape, some other equally appropriate dimension would be used. Most of the pores however, are irregularly shaped and an arbitrary definition of *pore size* is the only option. In addition, every material comprises of pores of a range of sizes, commonly referred to as the pore size distribution. Thus a practical definition of *pore size* must allow a large number of pores to be examined fairly rapidly.

_Pore size_ is expressed either in terms of the diameter (or radius) of the opening, assuming it is cylindrical or spherical, or simply as the width between planar sheets. Pores of widths less than 2 nm are referred to as micropores, whereas those having widths from 2 to 50 nm are called mesopores. Pores of larger widths than 50 nm are called macropores.\(^90, 97\)
3.1.4.3 $N_2$ and $CO_2$ adsorbives

Gas adsorption measurements, particularly $N_2$ at 77 K and $CO_2$ at 273 K, are used to obtain isotherm data that can be used to determine PSD. As previously mentioned, the main advantage of using $N_2$ as an adsorptive is that it spans a wide range of relative pressures, i.e. from $10^{-9}$ to 1 bar, resulting in a PSD that covers the whole range of porosity. $N_2$ adsorption data has been documented to supplement $CO_2$ data so as to provide a more complete picture of the porous structure of microporous materials. The existence of diffusional problems in the narrow porosity region ($< 0.7$ nm) severely limits the usefulness of $N_2$ adsorption as a characterisation tool for microporous materials. In order to circumvent this problem, use of $CO_2$ at 273 K and 303 K is proposed. $CO_2$ adsorption at 303 K is known to be complex due to the closeness of the temperature to the critical temperature of $CO_2$ (303 K). Despite its general experimental convenience and simple molecular structure, $CO_2$ sorption is complicated by the high quadrupole moment (about $1.1 \times 10^{-39}$ C cm$^2$). This makes the adsorption isotherm sensitive to the presence of polar groups in the adsorbate surface resulting in a wide variation of the monolayer surface. Thus $CO_2$ has been used in systems where there is no possibility of chemisorption.

Since the materials dealt with in this research are predominantly microporous, $N_2$ pore size distribution measurements tend to give inflated distributions at the low pore size region, e.g. $< 0.6$ nm. A more accurate distribution in this region can be obtained by complementing this with $CO_2$ pore size distribution data since $CO_2$ has been reported to be useful in the analysis of microporous materials with very narrow pores that cannot be accessed by nitrogen. This would however, be limited by the fact that, while the $N_2$ measurements are done at 77 K, the $CO_2$ data is obtained at a much higher temperature of 273 K, which is much higher than its boiling point of 195 K. Additional sorption data obtained using a gravimetric method at 303 K should complement this data as far as pore size distribution is concerned. The advantage of the IGA is that it can go to higher pressures than the ASAP, and thus cover a wider range of effective pore size.

The main advantage of $CO_2$ over $N_2$ is that, despite having similar molecular diameter as $N_2$ ($0.28$ nm for $CO_2$ and $0.30$ nm for $N_2$), the higher temperature gives it more kinetic energy so that it can penetrate into narrow micropores without experiencing diffusional problems. Consequently $CO_2$ yields microporosity data where $N_2$ is kinetically restricted.
The mechanism of adsorption in micropores is pore filling as opposed to surface coverage. Whereas N$_2$ at 77 K will condense in the pores at low $p/p^0$ (< 0.01), the state of CO$_2$ in the micropores is not clearly known. Some researchers suggest that at ambient and close temperatures, CO$_2$ will only form a monolayer on the walls of the pores, while others think it condenses to fill the pores. Lozano-Castello et al. obtained experimental data to prove that the adsorption mechanism for N$_2$ and CO$_2$ is similar and by condensation into the pores. This is micropore-filling.

3.1.4.4 Other adsorptives

In addition to N$_2$ and CO$_2$, there is a host of other adsorptives useful for characterising porosity. Some of these are outlined below.

(a) Argon

Argon is inert and made up of spherically symmetrical monatomic molecules. It is frequently used for sorption measurements at 77 K. Its physical properties, like boiling point, heat of vaporisation and polarisability, are fairly comparable to those of N$_2$. Thus Ar sorption is relatively easier to measure experimentally at 77 K, a temperature below the triple point (88.8 K). The inherent problem is in the value of $p^0$, whether to take the saturation vapour pressure of the solid or the supercooled liquid state. Literature uses the effective saturation vapour pressure as that of the supercooled liquid state ($p^0 = 220$ Torr at 77.2 K).

The disadvantage of using Ar in surface area measurement is that point B, which is the pressure and quantity adsorbed corresponding to the knee on the isotherm, is poorly defined, and the C value is low giving uncertainty in the monolayer capacity. B is the point on the isotherm corresponding to monolayer capacity, $V_m$, and C value represents the relative strengths of adsorption to the surface and condensation of pure adsorbate.

(b) Krypton

Because its saturation vapour pressure is low ($p^0 \sim 2$ Torr at 77 K), krypton can be used in the measurement of relatively low surface areas. The experimental temperature of 77 K is way below the triple point of Kr (116 K), and it is usual practice to use the saturation vapour pressure of the supercooled liquid ($p^0 = 2.49$
Torr at 77.35 K) as opposed to that of the solid. Besides the isotherm being difficult to interpret, the BET plot is usually not linear, which affects the value of the number of molecules on the monolayer.

(c) Xenon

Although xenon has a low saturation vapour pressure ($1.7 \times 10^{-3}$ Torr at 77 K), it is traditionally used for well-defined surfaces rather than for small surface areas. Xenon has a high polarisability (Chapter 4) compared to other adsorptives, thus its dispersion interactions with adsorbents should be large and a high degree of localisation is expected. Xe sorption is explored further in Chapter 4.
3.1.5 Pore size distribution models

There are a number of methods that are used for micropore analysis. These include the Horvath-Kawazoe (HK) model, improvements of the HK model, the Density Functional Theory (DFT), use of Positron annihilation lifetime spectroscopy, computer simulations and others. Among these, the HK model has been very widely used since its development in 1983. It is applicable to slit pores between parallel infinite graphite layers, and is by extension applied to PIMs because of the presence of aromatic rings in their structure. As a result this model is given a more extensive treatment here.

3.1.5.1 The Horvath-Kawazoe (HK) model

The Horvath-Kawazoe model is used to calculate the effective pore size distribution from the low pressure steep-rise region of a single gas adsorption isotherm for a microporous material. It is based on the relationship between micropore size and the adsorption potential energy of a gas molecule in a micropore of a given geometry. This relation derives from the mechanism of adsorption in micropores (≤ 2nm) which is assumed to be progressive pore filling rather than capillary condensation (as in the case of mesopores) or surface coverage. The underlying assumption of this model is that adsorbent pores can be treated as having slit-shaped graphitic geometry with the slit wall made up of two infinite slabs of graphite at a fixed distance apart. This has now been extended to apply to cylindrical and spherical pores as well. Since the filling of ultra-micropores is expected to occur at low relative pressure \( p/p^0 \), in order to investigate the first stages of micropore filling it is necessary to work at \( p/p^0 < 10^{-5} \).

The potential energy of interaction between one adsorbate molecule at a distance \( r \) from a single infinite-layer plane of adsorbent molecules is given by the 10:4 potential as follows:

\[
\varepsilon(r) = K_\varepsilon \left[ -\left( \frac{\sigma}{r} \right)^4 + \left( \frac{\sigma}{r} \right)^{10} \right]
\]

where
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\[-\left(\frac{\sigma}{r}\right)^4\] is the attraction term, and \[\left(\frac{\sigma}{r}\right)^{10}\] is the repulsion term,

\[
K = \left(\frac{n}{n-m}\right)^{-m} \left(\frac{n}{m}\right)^{m(n-m)}
\]

and \(\sigma\) is the gas solid nuclear separation at zero interaction energy, and is given by \[\sigma = d \times \left(\frac{m}{n}\right)^{\frac{1}{n-m}}\]. The constants \(n\) and \(m\) are the indices of the dispersion and repulsion terms respectively, so that \(n = 10\), and \(m = 4\).

Assuming that micropores are slits between two graphitised carbon layers, it is reasonable to extend this to two parallel infinite graphite planes with an inter-nuclear distance, \(L\), apart, yielding Equation 3.26 below:

\[
\varepsilon(r) = K\varepsilon^* \left[-\left(\frac{\sigma}{r}\right)^4 + \left(\frac{\sigma}{r}\right)^{10} - \left(\frac{\sigma}{L-r}\right)^4 + \left(\frac{\sigma}{L-r}\right)^{10}\right] \tag{3.26}
\]

Horvath and Kawazoe\(^8^4\) proposed that the potential in the micropores is increased by the interaction of adsorbate molecules within the pore. To account for this, an additional adsorbate dispersion term, \(N^*_a A^*_a\), is included so that:

\[
\varepsilon^* = \frac{3}{10} \frac{N^*_a A^*_a + N^*_s A^*_s}{d^4} \tag{3.27}
\]

Rearranging the expression for \(\sigma\) gives \(d = \sigma \times \left(\frac{2}{5}\right)^\frac{1}{6}\). Substituting for \(\varepsilon^*\) (from Equation 3.27) and incorporating the expression for \(d\) into Equation 3.26 gives:

\[
\varepsilon(r) = \frac{N^*_s A^*_s + N^*_s A^*_s}{2\sigma^4} \left[-\left(\frac{\sigma}{r}\right)^4 + \left(\frac{\sigma}{r}\right)^{10} - \left(\frac{\sigma}{L-r}\right)^4 + \left(\frac{\sigma}{L-r}\right)^{10}\right], \tag{3.28}
\]

which is a profile that combines the adsorbate-adsorbent interaction with the adsorbate-adsorbate interactions. Integrating this expression over the free space in the slit-pore gives the average interaction energy, \(\bar{\varepsilon}(r)\) as follows:
This assumes, however, that an adsorbate molecule has a continuous distribution of positions it can occupy in the micropore – an assumption that Cheng et al.\textsuperscript{99} later contested. Substituting for $\varepsilon(r)$ in the above expression, and relating this average potential to the free energy upon adsorption,\textsuperscript{6} $RT \ln \left( \frac{p}{p^0} \right)$ where $R$ is the gas constant, gives the following energy balance:

$$RT \ln \left( \frac{p}{p^0} \right) = N_{AV} \cdot \overline{\varepsilon}(r) = N_{AV} \frac{N_s A_s + N_a A_a}{\sigma^4(L - 2d)} \times \left[ \frac{\sigma^4}{3(L - d)} - \frac{\sigma^{10}}{9(L - d)^9} - \frac{\sigma^4}{3d^3} + \frac{\sigma^{10}}{9d^9} \right]$$

(3.30)

where $d$ is the sum of the diameters of the adsorbate molecule and the adsorbent atom. From this expression the interaction energy of a molecule is indeterminate at $L = 2d$ since at that point the free space of the pore, $L - d_s$, equals the diameter of the adsorbate molecule, $d_a$ (Figure 3.4). Equation 3.30 uses the physical properties of the adsorbate and adsorbent couple to relate the relative pressure ($p/p^0$) to the pore size, $L$, i.e. pores of a particular size will fill at a certain relative pressure, and can be represented as:\textsuperscript{73, 84, 105, 110}

$$\ln \left( \frac{p}{p^0} \right) = \frac{A}{L - d} \left( \frac{B}{\left( L - d \frac{2}{2} \right)^3} - \frac{C}{\left( L - d \frac{2}{2} \right)^9} - D \right)$$

(3.31)

where: $A = \left( \frac{N_{AV} \times IP}{RT \sigma^4} \right)$, $N_{AV}$ is the Avogadro’s number, $B = \frac{\sigma^4}{3}$, $C = \frac{\sigma^{10}}{9}$, and $D = \frac{\sigma^4}{3 \left( d \frac{2}{2} \right)^3} - \frac{\sigma^{10}}{9 \left( d \frac{2}{2} \right)^9}$, $IP$, the interaction parameter, is given by the expression: $IP = N_s A_s + N_a A_a$. 

$$\overline{\varepsilon}(r) = \frac{\int_{L-d}^{d} \varepsilon(r) dr}{\int_{d}^{L-d} dr}$$

(3.29)
$N_a$ is the number of molecules per unit area of the adsorbate, $N_s$ is the number of atoms per unit area of surface, $A_a$ and $A_s$ (erg cm$^6$) are the corresponding Lennard-Jones constants$^{76, 99, 107}$ expressed by the Kirkwood-Muller formalism$^{85, 106, 109, 110}$ as shown in Equations 3.32 and 3.33:

$$A_s = \frac{6mc^2\alpha_a\alpha_s}{(\frac{\alpha_s}{\chi_s}) + (\frac{\alpha_a}{\chi_a})} \quad (3.32)$$

$$A_a = \frac{3mc^2\alpha_a\chi_s}{2} \quad (3.33)$$

where $m$ is the mass of an electron, $c$ is the velocity of light, $\alpha_a$ is the polarisability and $\chi_a$ is the magnetic susceptibility of an adsorbate atom, $\alpha$ and $\chi$ are the polarisability and magnetic susceptibility of the adsorbent atom. Literature values of these physical properties are shown in Table 3.1. Clearly then, the Horvath-Kawazoe model provides a transformation of the physisorption data at low relative pressure into micropore sizes.

In the HK equation (Equation 3.30) $L$ is the distance (nm) between the nuclei of the two layers such that $L > d$. The effective pore width is $L − d$. The relationship between the adsorbate and adsorbent diameters is illustrated in Figure 3.4.
Figure 3.4 Diagrammatic representation of molecules adsorbed in a slit pore.\textsuperscript{105}

Table 3.1 Physical properties for calculating model parameters

<table>
<thead>
<tr>
<th></th>
<th>C (nm)</th>
<th>N(_2) (nm)</th>
<th>CO(_2) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter, (D) (x10(^{-24}) cm(^3))</td>
<td>0.34(^{a,b})</td>
<td>0.30(^{a,b})</td>
<td>0.323(^{b})</td>
</tr>
<tr>
<td>Polarisability, (\alpha) (x10(^{-24}) cm(^3))</td>
<td>1.02(^{a,b})</td>
<td>1.46(^{a})</td>
<td>1.76(^{b})</td>
</tr>
<tr>
<td>Susceptibility, (\chi) (x10(^{-29}) cm(^3))</td>
<td>13.5(^{a,b})</td>
<td>2.0(^{a})</td>
<td>3.6(^{b})</td>
</tr>
</tbody>
</table>

\(^a\)Data obtained from Reference 73. \(^b\)Data obtained from Reference 84.
3.1.5.2 Problems with the Horvath-Kawazoe (HK) model

The original HK equation\(^8\),\(^1\) considered a graphitic slit-shaped pore with an implicit assumption that the adsorption isotherm follows Henry’s law (linearity). This however, goes against the principle of the Dual Mode approach as discussed in section 3.1.3.2, since the latter model maintains that at low pressure the adsorption follows Langmuir mode while the Henry mode only becomes more pronounced at higher pressures.

In addition, the adsorbate-adsorbate-adsorbent interaction term, \(N_aA_a + N_sA_s\), is contestable because, according to Yang et al.\(^9\), there is no theoretical justification for incorporating these interactions in the HK equation.

Equation 3.30 basically says that the potential energy is the sum of the potential due to adsorbate-adsorbent interactions and that due to adsorbate-adsorbate interactions, that is:

\[
\varepsilon(r) = \varepsilon_{a-s}(r) + \varepsilon_{a-a}(r)
\]

Since \(r\) is the same for adsorbate and the adsorbent, this means that adsorbate-adsorbate interactions are due to a gas molecule and two parallel infinite sheets of gas molecules placed at the same position as the adsorbent molecules. This cannot be the case and is clearly a contradiction.

Additionally, in order to obtain \(\overline{\varepsilon}(r)\), the average potential energy, Equation 3.29 was used.

This implies a gas molecule has a continuous distribution of positions which it is free to occupy in the filled micropore. But, in reality, the gas molecule has only fixed positions at which it can exist when the pore is filled to capacity. The Boltzmann law of distribution of energy requires that the average energy should be calculated by using the weighted energy terms with the probability of a molecule to that energy, ie. \(\exp(-\varepsilon/kT)\). The molecule is thus expected to occupy a position where energy is a minimum.
Equation 3.30 is valid for the relative pressure range \( p/p^0 \geq p_c/p^0 \), where \( p_c/p^0 \) is the relative pressure corresponding to \( L = 2d \). When \( L = 2d \), the equation is indeterminate. But, of course, a finite value for the potential energy exists for a molecule of this size.

The Horvath-Kawazoe model further assumes isotherm data follows Henry’s law, which says the fraction of surface covered by an adsorbate, \( \theta \), varies linearly with the pressure of adsorption, as described by Equation 3.5.

Owing to these conceptual flaws, there is enough motivation to modify the model to be able to characterise the porosity of microporous materials adequately.
3.1.5.3 Modifications to the HK Model

New models have been proposed based on the same principles as the HK model, to include pores with curved surfaces. Prominent among them are the cylindrical-pore model by Saito and Foley and the spherical pore model due to Cheng and Yang.

(a) The Cheng-Yang Correction

In order to correct for the deviation of isotherm data from Henry’s law (Equation 3.8) at higher relative pressures, Cheng and Yang proposed a correction factor, which incorporates a Langmuir isotherm fit to the data. The Cheng-Yang correction factor essentially corrects for the nonlinearity of the isotherm. It incorporates an additional term to the HK equation for different geometrics, so that the corrected equation becomes Equation 3.35.

\[
\ln\left(\frac{p}{p^0}\right) = \frac{\epsilon}{\theta} - \left[1 - \frac{1}{\theta} \ln\left(\frac{1}{1 - \theta}\right)\right] \quad (3.35)
\]

where \(\frac{\epsilon}{\theta}\) is the HK equation (Equation 3.30). Equation 3.35 shall be referred to as the HK-CY equation henceforth. At high pressure the average interaction energy thus tends to that given in Equation 3.35. Near the saturation pressure, the size of the largest pore, which can be filled with adsorbate tends to infinity. As can be deduced from Equation 3.30, as \(L \to \infty\), the average interaction energy tends to zero. It is also apparent that there will always be adsorbate-adsorbate interactions even at very large pore widths, making the original model for the average interaction energy inconsistent with the HK-CY correction. The new model is supposed to have better agreement with crystallographic data in this respect.

(b) The Ross-Olivier parameter

Use of the Ross-Olivier parameter (which uses a lower value of the magnetic susceptibility for \(C\) of \(1.05 \times 10^{-29}\) cm\(^3\) instead of \(1.35 \times 10^{-28}\) which is used in the HK slit pore geometry, and effectively lowers the interaction parameter to \(2.61 \times 10^{-43}\) ergs cm\(^4\)) underestimates the pore widths. It is possible to use it with either the cylindrical pore or the spherical pore geometries.
Sorption of Gases and Liquids by Polymers of Intrinsic Microporosity (PIMs)

3.1.5.4 Alternatives to the HK model

Apart from modifications to the HK model, other independent models can be used. These include the Barette-Joyner-Halenda (BJH) method, the Density Functional Theory (DFT), and the Dubinin-Astakhov (DA) approach. Molecular simulations can also be used to predict pore size distributions.

(a) The BJH Method

The BJH method depends on a cylindrical pore condensation model\textsuperscript{19, 73} and is summarised by the correlation between pore radius, $r_p$, the Kevin radius, $r_K$, the molecular layer thickness, $t$, and the relative pressure, $p/p^0$. Equation 3.36, which is a combination of the Halsey equation and the Kevin equation\textsuperscript{73} shows how these parameters are combined to give a pore size distribution\textsuperscript{111} using $N_2$ at 77 K as an adsorptive.

$$r_p = -\frac{0.415}{\log(p/p^0)} + t \quad (3.36)$$

The BJH method is useful in characterising mesoporous materials, i.e. materials with porosity between 2 – 50 nm pore widths.\textsuperscript{112} Because the materials studied here are chiefly microporous, this model would be severely limited if used in characterising micropores, as will be demonstrated later.

(b) Density Functional Theory (DFT)

The Density Functional Theory (DFT) is a statistical based thermodynamic approach that assumes a system consisting of a single pore represented by two graphitic parallel walls separated by a fixed distance. The open pore is immersed into the adsorptive at a certain temperature and pressure. Under such conditions, the adsorptive molecules interact with each other as described by the Lennard-Jones potential (Equation 3.32 and Equation 3.33) and with the pore walls and reaches an equilibrium distribution. At this stage, the chemical potential at every point equals the chemical potential of the bulk of the adsorptive. This bulk is homogenous with a constant density; its chemical potential being determined by the pressure of the system. Near the walls the adsorptive density is inhomogeneous; its chemical potential comprises of several location-dependent contributions whose cumulative sum at every point equals the chemical potential.
of the bulk adsorptive. At equilibrium, the whole system has a minimum Helmholtz free energy. DFT describes this Helmholtz free energy as a function of the single-particle density distribution; therefore, calculating the density profile that minimizes it yields the equilibrium density profile. The pore size distribution is obtained by calculating many isotherm pressure points for a wide range of pore sizes using computer algorithms. This model is applicable down to 400 nm pore widths. However, as with the HK model, the DFT model is based on slit pores with graphite interaction energies.

(c) The Dubinin-Astakhov Model

The Dubinin-Astakhov theory of volume filling of micropores (TVFM) is expressed by the formulation in Equation 3.37.\textsuperscript{73, 113, 114}

\[
\log(V) = \log(V_0) - \left( \frac{RT}{\beta E_0} \right)^N \times \left( \frac{p^0}{p} \right)^N
\]  

where \( V \) is the volume adsorbed at equilibrium pressure (cm\(^3\) g\(^{-1}\) STP), \( V_0 \) is the micropore capacity (cm\(^3\) g\(^{-1}\) STP), \( E_0 \) is the characteristic energy (kJ/mol) \( N \) is the Astakhov exponent, and \( \beta \) is the affinity coefficient of the adsorptive relative to the \( p^0 \) gas.

While \( \beta \) depends only on the adsorptive, \( E_0 \) and \( N \) depend on the microporous system. The value of \( N \) varies from 1.5 to 3, but because of inaccuracies in the value from 2.5 to 3, a value of 2 is conveniently chosen for activated carbons and related materials. This value, however, assumes a homogenous system of micropores although it has been applied to heterogeneous systems as well.\textsuperscript{115} It is further assumed that \( E_0 \) varies inversely with pore width. The DA approaches requires the PSD shape (usually Gaussian) to be assumed. This unduly constrains the PSD calculation. In addition, TVFM is not applicable at low pressure, thus restricting the method.
(d) Molecular simulations

Along with the efforts to synthesise novel microporous materials, there is ongoing research that models the adsorption of hydrogen and other adsorptives. Because conventional PSD methods either underestimate or overestimate the mean pore width, and can sometimes fail to reveal the bimodal nature of the distribution, use can be made of molecular simulation methods. Conventional methods are also disadvantaged by the limited understanding of how adsorbate molecules behave in micropores and hence poor descriptions of the pore size distributions. Consequently, pore size distributions are model dependent. The molecular simulation approach has been thought to provide a solution to these problems by giving more information on the impact of pore size on adsorption that define the limits of the conventional methods and show the limitations of volume-filling models.

Hydrogen adsorption in graphite nanofibers (GNFs) has been modelled using the grand canonical Monte Carlo (GCMC) simulation for example. This treated the pores as slits bounded by layers of planar graphitic sheets. Hydrogen adsorption was modelled as two Lennard-Jones sites, and the interaction between a site and the graphitic surface was modelled on the basis of dispersion forces.

Molecular simulations have also been used to show that the density of adsorbed nitrogen in the micropores differs from that of liquid nitrogen.
3.2 Gas sorption method validation

Generally, an analytical method should be validated with respect to its limit of detection (LOD), precision and accuracy. Substantial literature has been dedicated to the validation of analytical methods that deal with well-defined analytes in solution. Horwitz observed a power-law trend that demonstrated that the repeatability of analytical measurements largely depends on the concentration of the analyte. He came up with the HoRat ratio, which is a normalised performance parameter that indicates the acceptability of analytical methods with regard to reproducibility.

In the case of gas sorption measurements where the ‘analyte’ is not as well-defined, this becomes problematic. It is, however still possible to determine parameters such as precision, accuracy, and limit of detection. Badalayan et al. used standard reference materials (SRMs) to evaluate the accuracy of automated gas adsorption apparatus. The traditional collaborative trials or, using the more correct IUPAC terminology, the inter-laboratory method performance study is also a useful practice in ascertaining the validity of analytical methodology.
3.2.1 Statistical approach

3.2.1.1 Precision

Precision is the agreement between two or more independent test results obtained under specified conditions. It describes the reproducibility of results of measurements that have been performed in exactly the same way. Precision thus means producing reliable and repeatable results. Parameters usually used to describe precision are sample standard deviation \( s \), variance \( s^2 \), and coefficient of variation \( CV \) as given by Equations 3.38 (a) and (b).

\[
s = \sqrt{\frac{\sum (x_i - \bar{x})^2}{N-1}} \quad \text{(a)}
\]

\[
CV = \frac{s}{\bar{x}} \times 100 \quad \text{(b)} \quad (3.38)
\]

Where \( x_i \) is the \( i^{th} \) out of a total of \( N \) measurements, and \( \bar{x} \) is the sample mean.

The precision and accuracy of experimental results is affected by random errors. Accuracy being the closeness of a result to the expected value. These follow a normal distribution and error is minimised by increasing the number of repeat measurements.

The statistic relative standard deviation (RSD) is usually used for assessment of results because it is often constant or linear with the measured quantity over a wide range.

3.2.1.2 Accuracy

The accuracy of an experimental result is its correctness or closeness to the true or expected value. Thus accuracy depends on the expectations of the scientist.

The accuracy of results is affected by systematic errors or bias, which are either instrument, person or method caused. Systematic instrument errors are corrected by calibration while personal errors are minimised by discipline and care. Method
validation, which includes the use of SRMs, is designed to minimise method errors.

The acceptance limits of results were established by means of Equation 3.39 (a) and (b):

Upper limit = \( \bar{x} + 2s \) (a) Lower Limit = \( \bar{x} - 2s \) (b) \hspace{1cm} (3.39)

3.2.1.3 Z-score values

The standardised value (Z-score), is an indication of the performance of the laboratory, showing as satisfactory, questionable or unsatisfactory. For each measurement, the laboratory Z-score is calculated from the laboratory mean result, the specified standard reference material result \((\mu)\), and the standard deviation of the specified result \((\sigma)\) using Equation 3.40.

\[
Z_i = (\bar{x}_i - \mu) / \sigma
\]  \hspace{1cm} (3.40)

From the Z-score, if \(|Z| \leq 2\) the results are satisfactory, if \(|Z| > 3\) the results are unsatisfactory, and if \(2 < |Z| < 3\) the results are questionable. The criterion for acceptance is that the mean is considered satisfactory if it is located between both limits.\(^{119}\)
3.3 Experimental

3.3.1 Gas sorption measurements

3.3.1.1 Accelerated Surface Area and Porosimetry (ASAP) measurements

Sorption isotherms were collected as described in Chapter 2. Micropore distributions were determined from $\text{N}_2$ adsorption data by the Horvath-Kawazoe (HK) method, assuming slit pore geometry and the original HK carbon-graphite interaction potential using the manufacturer’s software. The instrumental conditions for various materials are indicated in Table 3.2.

Table 3.2 ASAP Instrumental conditions for adsorption measurements

<table>
<thead>
<tr>
<th>Material</th>
<th>Gas</th>
<th>Degas time (h)</th>
<th>Temperature a (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Automatic</td>
<td>Manual</td>
</tr>
<tr>
<td>PIMs and related materials*</td>
<td>$\text{N}_2$</td>
<td>16</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>$\text{CO}_2$</td>
<td>16</td>
<td>24</td>
</tr>
<tr>
<td>Organic Crystal**</td>
<td>$\text{N}_2$</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>$\text{CO}_2$</td>
<td>10</td>
<td>10</td>
</tr>
</tbody>
</table>

a used an in-built heating mantle, b used liquid nitrogen, c used an external chiller annexed to the instrument.

* These include co-polymers, triptycenes.

** $3,3',4,4'$-Tetra(Trimethylsilyl ethynyl) biphenyl.

3.3.1.2 Sorption measurements on PIM-1 Films

An aliquot of the dried film was transferred into a sample tube and attached onto the auto-degas port. This was outgassed at 120 °C for 16 h, removed and reweighed before being transferred to the analysis port where it was manually outgassed at 120 °C overnight. Thereafter it was exposed to the adsorbate gas and an isotherm collected. A freespace measurement was performed at the end of
the analysis. The same procedure was carried out for N$_2$ and CO$_2$ except that N$_2$
sorption was performed at 77 K whereas CO$_2$ sorption was at 273 K.

3.3.1.3 IGA measurements

To complement the ASAP 2020 data, H$_2$ and some of the CO$_2$ measurements were
carried out using the Hiden Isochema (Warrington, England) Intelligent
Gravimetric Analyser (IGA).\textsuperscript{123} This is equipped with a microbalance that
measures weights to a resolution of ±0.2 mg, a water thermostat bath, and has
an operation pressure that ranges from ultrahigh vacuum (10$^{-6}$ bar) to 20 bar.
Before sorption analysis, the sample (about 60 mg) was loaded into a glass
sample holder, the temperature ramped at 2 K min$^{-1}$ from room temperature to
393 K, and degassed under ultrahigh vacuum (10$^{-6}$ bar) for 8 h. CO$_2$ sorption and
desorption measurements were carried out at 303 K using standard procedures,
as outlined in reference 123. Measured masses were corrected for buoyancy. The
density values were obtained by measuring the buoyancy (ca. 0.98 g L$^{-1}$) of the
sample in an inert gas, helium, as outlined below. The sample temperature was
set and maintained by means of a water bath to keep temperature fluctuations to
a minimum. The system then maintains the required pressure and monitors the
sample mass.

\textit{Buoyancy correction}

This follows the procedure outlined in reference 123 and referred to in reference
73. With the furnace power controller switched to the external position, the
sample enclosure was placed into a water jacket. The water temperature was set
to 303 K using a thermostat. An inert gas, helium, was turned on and when the
water bath temperature reached 303 K, the change in weight was measured over
a range of pressures up to 20 bar. Assuming that the interaction between the
polymer and the helium is negligible in comparison with the amount of helium
displaced by the polymer, the buoyancy correction factor was obtained and
incorporated into the CO$_2$ sorption data.
3.3.1.4 Coulter measurements

After sample preparation as outlined in section 2.4.6.6, about 100 mg of the sample was transferred into a sample tube and attached to the degas port of the Coulter 3100. The sample was then degassed at 120 °C under vacuum (~10⁻⁴ bar) for 16 hours. After that it was reweighed and the sample tube attached to the analysis port and N₂ sorption performed at 77 K in a liquid nitrogen bath. The isotherm data was transferred to an excel file and the data treated as for ASAP 2020 using the algorithm described next.

Unlike the ASAP 2020, the IGA instrument software does not allow pore width data to be readily generated. Pore width data is generated by use of the Horvath-Kawazoe model (Equation 3.30), which requires certain physical parameters about the adsorptive and adsorbent to be known. A description of how this was achieved is summarised in the form of an algorithm below.

3.3.1.5 Algorithm for obtaining effective pore size of micropores

The following algorithm was used to obtain effective pore widths of micropores from IGA isotherms. Parameters that are temperature dependent (\( N_a \), \( p^0 \) for CO₂ and density conversion factor) are obtained by extrapolation from known values at known temperatures (Table 3.3), while the molar gas volume at 303 K was obtained by calculation using the ideal gas equation (Equation 3.41).

<table>
<thead>
<tr>
<th>( N_a ) (molec. cm⁻²)</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.58 x 10¹⁴</td>
<td>298</td>
</tr>
<tr>
<td>5.45 x 10¹⁴</td>
<td>273</td>
</tr>
<tr>
<td>7.69 x 10¹⁴</td>
<td>195</td>
</tr>
</tbody>
</table>

\( N_a \) at 303 K was estimated at 9 x 10¹³ molec. cm⁻².
p° was estimated using parabolic data shown in Table 3.4.

<table>
<thead>
<tr>
<th>p° (mmHg)</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>164</td>
</tr>
<tr>
<td>400</td>
<td>187</td>
</tr>
<tr>
<td>3800</td>
<td>216</td>
</tr>
<tr>
<td>15200</td>
<td>254</td>
</tr>
<tr>
<td>45600</td>
<td>295</td>
</tr>
</tbody>
</table>

This closely matches the value supplied by Micromeritics.

To obtain the density conversion factor for CO₂ at 303 K, the data in Table 3.5 was used.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Density Conversion Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>273</td>
<td>1.8306 x 10⁻³</td>
</tr>
<tr>
<td>298</td>
<td>1.935 x 10⁻³</td>
</tr>
</tbody>
</table>

The density conversion factor at 303 K was estimated at 2.015 x 10⁻³.

The molar gas volume, $V_m$, at 303 K was obtained by calculation from the ideal gas equation $(pV = nRT)$, from which

$$V_m = \frac{RT}{p} \quad (3.41)$$

Taking $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$, $T = 303 \text{ K}$, and $p = 100 \text{ kPa}$ (this is approximately 1 atm), this approximates $V_m$ at $25.1914 \text{ dm}^3 \text{ mol}^{-1}$.

1. Using the physical constants in Table 3.1, the values of $A_s$ and $A_a$ were calculated from Equations 3.32 and 3.33.

The value of $\sigma$ was calculated from the information defining Equation 3.25 and used to compute the interaction parameter ($IP$).

2. $A, B, C$ and $D$ were evaluated from the information defining equation 3.31.

3. The value of $N_a$ at 303 K was determined by extrapolation.

These model parameters gave the following expression from the HK model:
\[
\ln \left( \frac{p}{p^0} \right) = \frac{31.43}{L-0.663} \times \left[ \frac{2.181 \times 10^{-3}}{(L-0.3315)^3} - \frac{3.850 \times 10^{-7}}{(L-0.3315)^9} - 0.05191 \right] 
\]

(3.42)

5. A slit width \( L \) within the range \( L > 0.663 \) nm was conjectured.

6. \( L \) was substituted for in Equation 3.30 and the effective pore width, \( (L - d_a) \) together with the corresponding adsorbate relative pressure\(^1\), \( p/p^0 \), were calculated.

7. To obtain \( p/p^0 \) from IGA data, \( p \) was multiplied by 0.75 to convert from mmHg to bars, and divided by the saturated pressure of CO\(_2\) at 303 K (which in turn was obtained by extrapolation).

8. The \( p/p^0 \) value thus obtained was compared with \( p/p^0 \) from the IGA results data table. If \( p/p^0 \) matched the calculated value, the \( L - d_a \) value was taken as the effective pore width at that relative pressure. Else, a new \( L \) was guessed and iterated from 6 above.

9. The density conversion factor and the molar gas volume at 303 K were estimated by extrapolation.

10. The volume adsorbed was calculated by multiplying the molar uptake by the molar gas volume at 303 K.

11. The cumulative pore volume was calculated by multiplying the volume adsorbed by the density conversion factor.

12. A plot of the 5-point slope, \( dV/dw \), against pore width gave the PSD.

For \( N_2 \), two sets of physical constants are available in literature\(^84,105,106,110\) (Table 3.7) and as a result they yield two sets of IP and hence parallel PSD data. On the one hand, using an \( \alpha_a \) value of 1.46 x \( 10^{-24} \), and a \( \chi_a \) value of 2.00 x\( 10^{-29} \), an IP value of 3.73 x \( 10^{-43} \) erg cm\(^4\) was obtained. This reduces the HK model to:

\(^1\) \( p/p^0 \) for CO\(_2\) at T>195 K is only a theoretical parameter without much physical significance.
This is consistent with data reported by Roquerol et al.\textsuperscript{19} On the other hand, using an $\alpha_\alpha$ value of $1.76 \times 10^{-24}$, and a $\chi_\alpha$ value of $3.60 \times 10^{-29}$, an $IP$ value of $6.53 \times 10^{-43}$ erg cm$^4$ gives an $A$ value of 108.10, which generates PSD data that agrees with the ASAP instrument settings.\textsuperscript{73} It seems reasonable to use this set of physical constants for consistency and comparability of data. The corresponding HK formula is:

$$\ln \left( \frac{p}{p^0} \right) = \frac{108.10}{L - 0.64} \times \left[ \frac{1.894 \times 10^{-3}}{(L - 0.32)^2} - \frac{2.205 \times 10^{-7}}{(L - 0.32)^6} - 0.0512 \right]$$

For CO$_2$ however, two sets of data arise because adsorption isotherms were obtained at two different temperatures using two different techniques (ASAP, 273 K; IGA, 303 K). Two $IP$ values were consequently calculated, each for the respective temperature. Table 3.6 lists the calculated values of the different parameters.

### Table 3.6 Evaluating parameters in the HK equation

<table>
<thead>
<tr>
<th>Adsorbate gas</th>
<th>$N_2$</th>
<th>CO$_2$*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, K</td>
<td>77</td>
<td>273</td>
</tr>
<tr>
<td>$IP$ (x $10^{-43}$ erg cm$^4$)</td>
<td>3.73</td>
<td>6.53</td>
</tr>
<tr>
<td>$A$</td>
<td>61.78</td>
<td>108.10</td>
</tr>
<tr>
<td>$B$ (x $10^{-3}$)</td>
<td>1.894</td>
<td>1.894</td>
</tr>
<tr>
<td>$C$ (x $10^{-7}$)</td>
<td>2.705</td>
<td>2.705</td>
</tr>
<tr>
<td>$D$</td>
<td>0.05012</td>
<td>0.05012</td>
</tr>
</tbody>
</table>

$N_a$ at 303 K was estimated by extrapolation using literature values of $N_a$ at 195 K, 273 K, and 298 K. Although error is inherent in this value because linearity was assumed, it yields a value closer to the actual considering how close 298 K is to 303 K. The CO$_2$ vapour pressure at 303 K was estimated at $6 \times 10^4$ mmHg.
Thus from the mathematical treatment it is possible to compare experimentally obtained pore size distributions against those predicted by theory, and effect appropriate modifications to the calculated values in order to explain experimental data. MS Excel spreadsheets were designed to generate $p/p^0$ data from assigned values of pore width. Up to 3 decimal places, for every $p/p^0$ there exists a unique pore width value. On account of the extrapolations and small number of points involved, pore sizes obtained are only regarded as approximate.

For CO$_2$, the values differ with temperature as shown in Table 3.7 below.

Table 3.7 Variation of the relationship between pore width and pressure with measurement temperature for CO$_2$ sorption

<table>
<thead>
<tr>
<th>$p/p^0$</th>
<th>Pore width (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>273 K$^a$</td>
</tr>
<tr>
<td>5.55 x 10$^{-2}$</td>
<td>0.392</td>
</tr>
<tr>
<td>1.37 x 10$^{-4}$</td>
<td>0.423</td>
</tr>
<tr>
<td>1.83 x 10$^{-3}$</td>
<td>0.433</td>
</tr>
<tr>
<td>1.28 x 10$^{-2}$</td>
<td>0.687</td>
</tr>
<tr>
<td>9.91 x 10$^{-2}$</td>
<td>1.081</td>
</tr>
<tr>
<td>3.09 x 10$^{-1}$</td>
<td>1.856</td>
</tr>
<tr>
<td>3.80 x 10$^{-1}$</td>
<td>2.188</td>
</tr>
</tbody>
</table>

$^a$ Obtained using the ASAP, $^b$ Obtained using the IGA. The IGA does not generate pore width data, this is inferred from the spreadsheets of which this table is an extract.

3.3.1.6 H$_2$ sorption and the HK model

In order to apply the H-K model to the low pressure H$_2$ adsorption data, a number of assumptions have to be made. In addition to assuming that the adsorbent is comprised of infinite parallel sheets of graphite, it will be assumed that the mechanism of adsorption in the micropores is pore filling.

The number of H$_2$ molecules per unit area is required for the determination of the interaction parameter. This is obtained from Equation 3.45 by extrapolation of the $e^2$ versus atoms adsorbed plot$^{124}$ as illustrated in Figure 3.5.
\( \varepsilon^2 = \left[ RT \ln \left( \frac{p}{p^0} \right) \right]^2 \)  

(3.45)

**Figure 3.5 Determining the number of H\(_2\) molecules on a monolayer**

In order to calculate the interaction parameter the following physical parameters are used for H\(_2\).

**Table 3.8 Physical parameters used to compute the pore size distribution for H\(_2\)**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetic susceptibility (cm(^3))</td>
<td>6.71 x 10(^{-29})</td>
</tr>
<tr>
<td>Polarisability (cm(^3))</td>
<td>0.79 x 10(^{-24})</td>
</tr>
<tr>
<td>Hard sphere diameter (nm)</td>
<td>0.277</td>
</tr>
<tr>
<td>Number of molecules per unit area of adsorbent (cm(^2))</td>
<td>5.17 x 10(^{14})</td>
</tr>
</tbody>
</table>

Using Equations 3.30 and 3.31, the Leonard-Jones constant for H\(_2\), \( A_{H_2} \), is 6.51 x 10\(^{-66}\) J cm\(^6\). This gives a value of 8.21 x 10\(^{-43}\) erg cm\(^4\) for the interaction parameter.
3.3.2 Gas sorption methodology validation

Instrument calibration was performed periodically by Micromeritics Ltd, and each time the calibration file was reloaded to update the calibration before every measurement on the ASAP2020. A Carbon black reference material was used to check instrument performance. Thereafter, a standard zeolite sample (silica alumina 004/16821/00) was periodically used. Selected PIM samples were analysed (with the help of colleagues) on the ASAP2020, the Coulter 3100 and the ASAP2010 from our laboratory. Some, together with the standard zeolite material, were selected for proficiency testing for analysis on the Coulter 3200 by our collaborators at the University of Cardiff. Statistical techniques were used to correlate the data and determine key performance parameters like mean, standard deviation, coefficient of variance, and the Z-values of results.

Measurement procedure

Between 0.2 – 0.3 g of sample was evacuated at 90 °C for an hour, then at 350 °C for at least 4 hours. This was then tested following the procedure outlined in Chapter 2.
3.4 Results and Discussion

3.4.1 Optimisation of sample preparation and outgas procedures.

3.4.1.1 Sorption method validation

The BET surface area data for standard reference material SRM4 is presented in Table 3.9. There is reasonably good agreement between the different techniques for BET surface area between the different instruments. This is however, a relatively low surface area material. Despite the Coulter 1 and ASAP2020 mean values being close to the lower limit (203.0 m$^2$ g$^{-1}$), all the Z-values are within the satisfactory range ($|Z| \leq 2$). This means the method is plausible enough for the measurements undertaken on all the three instruments within the BET surface area range. There is still however, uncertainty towards extending this conclusion to measurements on higher surface area materials. Good agreement at low BET surface area does not necessarily guarantee the same at the high surface areas involved in PIMs. The unavailability of standard reference materials closely resembling high surface area microporous materials is the limiting factor.

<table>
<thead>
<tr>
<th>Instrument</th>
<th>N</th>
<th>$\bar{x}$ (m$^2$ g$^{-1}$)</th>
<th>S (m$^2$ g$^{-1}$)</th>
<th>%CV</th>
<th>Z-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coulter 1</td>
<td>5</td>
<td>203.7</td>
<td>2.5</td>
<td>1.2</td>
<td>-1.88</td>
</tr>
<tr>
<td>Coulter 2</td>
<td>2</td>
<td>226.6</td>
<td>12.3</td>
<td>5.4</td>
<td>+1.93</td>
</tr>
<tr>
<td>ASAP2020</td>
<td>3</td>
<td>204.7</td>
<td>1.8</td>
<td>0.9</td>
<td>-1.72</td>
</tr>
</tbody>
</table>

*Coulter 1 is the Manchester Coulter 3100, Coulter 2 is the Cardiff Coulter 3200, and ASAP 2020 is the Manchester ASP2020.*

To put the results into perspective, they are plotted together with results for high surface area materials (Figure 3.5). There is substantial agreement between the instruments for higher surface area materials as well.

Laboratory-to-laboratory variation is however expected. This is because every laboratory operates under different conditions of humidity, power supply, atmospheric pressure, instrument adjustments, and personnel operation.

An in-house comparison of the ASAP 2020 and Coulter 3100 at Manchester university shows close agreement between the BET surface area results as shown in Figure 3.6. The small difference for the PIM-1, PIM-2 and TAPIM-1 could be explained by the difference in operational vacuum for the two instruments. The
ASAP2020 is equipped with powerful turbo-molecular pumps capable of reaching very high vacuum ($10^{-8}$ bar), whereas the Coulter 3100 is only capable of up to $10^{-4}$ bar. The high vacuum in the ASAP therefore could be causing the microporous structure of the materials to collapse, especially for amorphous materials where the microporosity is not caused by a well-defined structure.

![Figure 3.6 BET surface area for different materials using the ASAP 2020 (red circles) and the Coulter 1 (blue diamonds). The red triangle is data obtained from Coulter 2.](image)

There is a significant difference between BET surface area for MeTripPIM obtained from the ASAP 2020 and Coulter 2. At this stage the reason(s) can only be speculative. Coulter 2 is a semi-automated version of Coulter 1, and their ranges of vacuum operation are the same. The ASAP 2020, being capable of reaching higher vacuum is likely to collapse the porous structure of the material. Laboratory-to-laboratory variation is expected. This is because every laboratory operates under different conditions of humidity, power supply, atmospheric pressure, instrumental adjustments, and personnel operations. This variation between the ASAP 2020 and Coulter 2 has motivated more collaborative study between the two sources culminating in the proposal of a common methodology. The ASAP 2020 subjects the sample to a ‘double degas regime’. The sample is auto-degassed for a 16 h period, followed by a 10 h manual degas. If the argument about high vacuum causing collapse of the microporosity is taken seriously, a reduction in the degas times and/or temperature is likely to reduce
this. Figure 3.7 shows a comparison of the same batch of PIM-1 (JDS057) degassed at different temperatures for different lengths of time.

![Figure 3.7 The variation of HK pore size distribution using N\textsubscript{2} (77 K) with degas time and temperature. Blue diamonds (8 h, 70 °C), red squares (10 h, 80 °C), black triangles (12 h, 100 °C), blue crosses (16 h, 120 °C).](image)

The degas at 120 °C for 16 h is the standard procedure, and it clearly shows for this sample that the N\textsubscript{2} probe is not able to access all the microporosity. The combination of degas temperature and time that allows the probing of most of the microporosity is a degas for 8 hours at 70 °C. Hence these milder outgas conditions will preserve the microporous structure so that it can be as fully characterised as possible. This is the proposed procedure for use with all the three instruments.

### 3.4.2 Determination of micropore distribution from N\textsubscript{2} adsorption at 77 K

Pore size distributions in porous materials can be determined using a number of data acquisition and manipulation techniques. These include the Barrett-Joyner-Halenda (BJH) method, the Density Functional Theory (DFT), the Dubinin-Astakhov approach, and the HK model.
3.4.2.1 Comparing models

In order to compare and validate the applicability of the PSD models, a well-defined crystalline material (as opposed to the amorphous PIMs) was used. Other researchers have used MS14, a zeolite. The material used in the present work, 3,3’,4,4’-tetra(trimethylsilylethynyl)biphenyl, was supplied by Kadhum Msayib who synthesised it as described in literature and crystallised it from concentrated hexane solution. N₂ sorption measurements were performed under the conditions given in Table 3.2. An outgas temperature of 333 K was used to prevent the material from decomposing at higher temperatures. The isotherm data were subsequently converted to a pore size distribution using the HK model. This was then compared with crystallographic data.

(a) 3,3’,4,4’-Tetra(Trimethylsilylethynyl)biphenyl

The low pressure region of the N₂ adsorption isotherm (Figure 3.8) for 3,3’,4,4’-tetra(trimethylsilylethynyl)biphenyl shows two distinct inflections which seem to correspond to the filling of the channels of 0.4 nm diameter and then, the 1.1 nm voids that the channels connect.

![Figure 3.8 An expansion of the low pressure region of the N₂ adsorption isotherm for 3,3’,4,4’-Tetra(Trimethylsilylethynyl)biphenyl showing two distinct inflection points. The full isotherm was shown in Figure 2.19.](image)

The low pressure region of the adsorption isotherm was analysed using the BJH model, the DA approach, DFT, and the HK model as shown in Figure 3.9.
The BJH model is only showing pore widths down to 1.7 nm. It therefore misses out the channels and voids within the crystal structure. The BJH model is useful for characterising mesopores, so that its application to micropores does not yield meaningful data.

The DFT approach shows two peaks which are not very well pronounced, one at about 0.6 nm and the other at around 1.9 nm. This is reasonably comparable to (1.1 nm voids linked by 0.4 nm channels) data that shows the existence of two types of holes observed in the 3,3′,4,4′-tetra(trimethylsilylethylene)biphenyl crystal using XRD. Despite this closeness of results, DFT yields data consistently higher than expected, and will therefore not be used any further in this work.

The DA approach is not sensitive to the quantity of N₂ gas adsorbed by pores less than 2 nm and cannot be overlayed meaningfully with the rest of the graphs. Because of this a separate plot of pore size distribution is shown in Figure 3.10. The modal pore width is also shifted to the right and does not correspond to the pore widths dictated by the geometry of 3,3′,4,4′-tetra(trimethylsilylethylene)biphenyl as elucidated by XRD. This PSD peaks off just above 2 nm making it inapplicable to microporous materials.

Analysis of this low pressure N₂ adsorption data using the Horvath-Kawazoe model⁷³, ⁸⁴ (assuming a slit-pore geometry and using a carbon-graphite potential) gives a bimodal pore size distribution. The well-defined peak at 1.1 nm corresponds to the maximum size of the voids within the crystal, consistent with crystallographic dimensions of 3,3′,4,4′-tetra(trimethylsilylethylene)biphenyl. An accurate modelling of the channels between the voids is not possible because the channels are too narrow; hence they are outside the range of the experimental method which is determined by the strength of the vacuum achievable with the turbo-molecular pumps the instrument uses.
Figure 3.9 N₂ (77 K) HK (blue diamonds), DA (red dots), DFT (black triangles), and BJH (purple squares) PSD for 3,3’,4,4’-tetra(trimethylsilylethynyl)biphenyl. The DFT oscillates between positive and negative values of dV/dw, and so the negative values have been omitted for purposes of overlaying the graphs for ease of comparison.

Thus the channels and voids in 3,3’,4,4’-tetra(trimethylsilylethynyl)biphenyl can be adequately characterised using the HK treatment of N₂ gas sorption data. Since there is such agreement between this model and XRD, it therefore is reasonable to infer that the HK model can be used, to an extent, to account for the microporosity in PIMs and related materials.
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Figure 3.10 The Dubinin-Astakhov PSD for 3,3',4,4’-tetra(trimethylsilylethynyl)biphenyl. This is shown separately because the pore volumes are too small to be overlayed onto the graphs in Figure 3.9.

**PIM-1**

The application of these models for PIM-1 N₂ sorption at 77 K is shown in Figure 3.11. It seems all the other approaches, except for the HK model cannot adequately account for the micropores in PIM-1.

Figure 3.11 N₂ (77 K) HK (blue diamonds), DA (red dots), DFT (black triangles), and BJH (purple squares) PSD for PIM-1
While modified versions of the HK model have enjoyed relative success when applied to activated carbons and clays, it appears none of these can adequately account for the microporosity of the materials under study. Ghosal et al. recommended use of the DA model to high pressure CO\textsubscript{2} sorption data. Perhaps this could be because of the amorphous nature of the polymers compared to the well defined structure of zeolites, for example. Sacchetti used the DFT approach in characterising the surface energy of \( \alpha \)-lactose monohydrate, a crystalline material with no micro- or mesoporosity. The way pore widths are defined for amorphous materials is such that the transient voids are approximated to well defined geometries.

Despite being the model of choice for characterising the microporous materials in this work, the HK model itself does not access micropores below 0.6 nm. This is thought to be an artefact of the measurement process, which only goes down to vacuum levels of \( 10^{-8} \) bar, a pressure that would correspond to a pore width within the range 0.58 – 0.65 nm. In order to characterise micropores below this range, measurement conditions have to be changed. This includes the choice of adsorptive (eg. CO\textsubscript{2} or H\textsubscript{2}), the strength of the vacuum (this might mean using a different type of instrument), and the temperature of measurement. This led to the following investigation in which CO\textsubscript{2} and H\textsubscript{2} were used as adsorptives. CO\textsubscript{2} measurements were undertaken at two different temperatures (273 K and 303 K), and H\textsubscript{2} sorption was carried out at 77 K.
3.4.3 Use of CO₂ and H₂ for pore size analysis

3.4.3.1 CO₂ sorption at 303 K and 273 K, and H₂ sorption at 77 K by PIM-1

A comparative representation of the pore size distributions of N₂ (77 K) and CO₂ (273 K and 303 K) data for PIM-1 is shown in Figure 3.12. The N₂ data peaks around 0.6 nm. This however, cannot be conclusive because a combination of (i) the physical properties of N₂ (its hard sphere diameter, diamagnetic susceptibility and polarisability), (ii) its interaction parameter with the idealised ‘graphite slabs’ of the PIM-1 adsorbent, and (iii) the instrument capability in terms of the lowest vacuum attainable, and the boundary conditions of the HK model (Equation 3.30) will make the N₂ PSD show a cumulative peak at a certain higher pore width. Any porosity below that shows at this larger value, indicating an apparent loss of porosity. The lowest vacuum the ASAP 2020 instrument can achieve is in the region of 10⁻⁸ bar.

![Figure 3.12 N₂ at 77 K (purple graph), CO₂ at 273 K (blue graph), CO₂ at 303 K (red dots), and H₂ at 77 K (triangles) PSD for PIM-1 (PIM-1 CO₂ at 303 K sorption data by Greg Larsen, Pennsylvania State University, H₂ sorption measurements were done by Steve Tedds, University of Birmingham)](image)

CO₂ sorption data shows that PIM-1 has lower microporosity than indicated by N₂ data. This is the ‘missing porosity’ that shows as a cumulative peak at about 0.65 nm for the N₂ PSD. In view of this, CO₂ studies can be used to complement N₂ data. Despite the investigations being carried out at different temperatures, these
two sets of data show that neither of the techniques will separately be able to elucidate the pore size distribution of the materials under study. Whereas N\textsubscript{2} data gives a peak around 0.6 nm, CO\textsubscript{2} peaks off at 0.65 nm. The two distributions however, meet at around 0.70 nm, which seems a reasonable estimate considering the aforementioned limitations of the N\textsubscript{2} technique.

Agreement between CO\textsubscript{2} PSD data obtained by two different methods at different temperatures, i.e. the ASAP 2020 volumetric analyser and the IGA gravimetric analyser, is novel and remarkable. The minor discrepancy could be because the IGA data were obtained at a higher temperature (303 K) compared to the ASAP2020 (273 K). At a higher temperature one would expect the CO\textsubscript{2} molecules to possess more kinetic energy as predicted by Boltzmann distribution and hence its diffusion properties are enhanced.\textsuperscript{112} In addition, it is possible that at the higher temperature of 303 K there is a general expansion of pore sizes which result in the PSD being consistently above that at 273 K.

Further insight into this phenomenon can be elucidated by considering the area under each of the CO\textsubscript{2} and N\textsubscript{2} PSDs as shown in Figure 3.13.

Figure 3.13 Pore Volumes for N\textsubscript{2} at 77 K (purple dots), CO\textsubscript{2} at 273 K (blue diamonds), and CO\textsubscript{2} at 303 K (red dots)

Figure 3.13 above basically compares cumulative pore volumes at a given pore width for the different adsorbives. The area under the curves converges at \( \sim 1.4 \) nm, showing that the N\textsubscript{2} peak is effectively probing into the same microporosity as CO\textsubscript{2}. Hence the N\textsubscript{2} peak in the PSD (Figure 3.13) is not real, but the cumulative effect of the micropores below 0.65 nm. This suggests that, although
the N₂ is accessing the pores below 0.65 nm, the HK model does not allow such pore widths to be ‘visible’ using N₂ as the probe molecule.

3.4.3.2 CO₂ sorption at 303 K and 273 K, and H₂ sorption at 77 K by PIM-7

The robustness of the approach that uses CO₂ and N₂ sorption data to complement each other is further demonstrated in PIM-7. The relationship between CO₂ and N₂ PSD data that was seen with PIM-1 data is fairly replicated here (Figure 3.14), and the PSD data peaks at around 0.7 nm.

Although some researchers argue that the sorption of CO₂ cannot be compared directly to that of N₂ owing to the different experimental conditions,²⁵ the following deductions can be made. From the above PSD graphs (Figure 3.14), besides the fact that the materials analysed adsorb a significant amount of CO₂ and N₂, there is a consistent trend in the way CO₂ PSD at 273 K relates to PSD at 303 K and to N₂ PSD. Again, the peak shown by the N₂ PSD does not seem to be real. It appears to be the cumulative effect of pores of sizes below and up to 0.6 nm.

The choice of physical parameters is critical in comparing data from different adsorbents. This is because the pore size is sensitive to small variations in the physical parameters used.⁸⁵
Because of the simplifying assumptions and hence conceptual flaws in the derivation of the Horvath-Kawazoe equation, the model might not adequately account for the porosity of materials studied herein. Rege et al.\textsuperscript{105} argue that the HK model underestimates the total interaction energy of the adsorbate and highly underestimates the PSD. They proceeded to propose a corrected model which agrees closely with crystallographic data. However, the original HK model is still in wide use due to its relative simplicity and it also is the first stage in the development of a unified theoretical approach on the filling of micropores.\textsuperscript{19}

Hydrogen sorption by both PIM-1 and PIM-7 under the experimental conditions does not seem to access pores below 1 nm. Despite having a smaller hard core radius of 2.77 nm compared to that of N\textsubscript{2} (3.15 nm) and CO\textsubscript{2} (3.23 nm),\textsuperscript{84} H\textsubscript{2} has the largest magnetic susceptibility out of the three adsorbatives. This affects the mechanism of interaction between H\textsubscript{2} and the polymer in the pores. Because this mechanism has not been pursued in this work, an explanation can only be speculation. N\textsubscript{2} for example, has been known to have enhanced interactions with zeolites so that discriminating between different zeolites would be impossible.\textsuperscript{112} It might thus be possible that, as H\textsubscript{2} is adsorbed into the polymer pores it gets tangled up in hydrogen bonding through cooperative adsorbate-adsorbent interactions\textsuperscript{127} and builds up a heel that constricts the cavities.

3.4.3.3 Comparing the HK model and modifications to the HK model

A comparison of the HK model (slit pore geometry), the HK with Cheng Yang correction, HK with the Ross-Olivier parameter, and the Ross-Olivier (spherical geometry) models for N\textsubscript{2} sorption by PIM-1 is shown in Figure 3.15.
Figure 3.15 N\textsubscript{2} (77 K) PSD for PIM-1 using the original HK slit-pore geometry (red dashes), HK with the Ross-Olivier parameter (blank diamonds), the Ross-Olivier cylindrical geometry (purple stars), the Ross-Olivier spherical geometry (brown dots), Dubinin-Astakhov (blue triangles), Saito-Foley (pink crosses), HK with spherical geometry (blue crosses)

Clear agreement is evident between the results of the HK and the HK-CY PSD calculations. A slit-pore geometry with the original HK interaction parameter gave similar results to the cylinder pore geometry (Saito-Foley)\textsuperscript{85} with the Ross-Olivier interaction parameter. This was also found to be consistent with the results obtained for organic crystal. Similar observations were made by Heuchel et al\textsuperscript{116}.

The DA PSD peaks around 1.5 nm pore width. This value is a lot higher than the 0.65 – 0.75 nm range obtained with the HK model on both CO\textsubscript{2} and N\textsubscript{2} adsorption data. It thus appears the model overestimates the pore widths. Ghosal et al.\textsuperscript{126} have recommended the use of the DA model to high pressure adsorption data, that is, up to 28 atm.
(b) Computer Simulations

A superimposition of Figure 3.12 onto computer simulation data for PIM-1 obtained by Heuchel\textsuperscript{116} is shown in Figure 3.16. The HK distribution shows a modal pore width in the region 0.6 – 1.0 nm. This is expected for a microporous material. A direct comparison with computer simulated data is limited by the different quantities used to characterise the pore size. On the one hand the HK model used the shell-to-shell distance as the pore width, while in computer simulations a volume element is first defined and converted mathematically to pore width values. Despite this difference however, Figure 3.16 shows a close agreement between pore size distributions generated by the two approaches.

![Figure 3.16 PSD comparison between computer simulations (bar chart), N2 at 77 K (purple graph), CO2 at 273 K (blue squares), and CO2 at 303 K (red dots) for PIM-1. (Molecular simulation data was obtained from reference 116).](image-url)
3.4.4 Effect of sample form on gas sorption behaviour: comparison of film with powder

N₂ sorption measurements were performed on films as well as powders of PIM-1 in order to investigate the effect the form of the material has on sorption behaviour.

Acquisition of a N₂ isotherm for PIM-1 films took much longer than that for powder material. Significant hysteresis upon desorption of N₂ was observed (Figure 3.17). There is a possibility that the polymer changes its morphology as the gas pressure is increased. Condensation within the pores could also have the same effect.²⁵ Weber et al.¹²⁸ reported structural changes accompanying helium adsorption at room temperature. Similar hysteresis behaviour has been observed on hydrogen adsorption in flexible metal-organic frameworks.⁷ Kinetic effects could also play a part. These might arise as very tiny micropores adapt themselves to fit the adsorptive molecular sizes.¹⁰³

![Figure 3.17 PIM-1 powder and film N₂ (77 K) sorption. Slow sorption kinetics evident on the film isotherm (red diamonds) and swelling of polymer could be responsible for the rather large hysteresis loop.](image)

The accessible microporosity of PIM-1 is significantly reduced upon film formation. It appears the film-forming process is accompanied by blanking of some pores which become tortuous and ‘blind’ and hence difficult to access. N₂ diffusion into very narrow pores is very slow due to the low kinetic energy²⁵ of N₂ at 77 K. The tortuosity appears to decrease as the relative pressure increases so that smaller pore sizes appear at a higher relative pressure where larger pores are expected
to appear. The surface area exposed to the N₂ gas is also very low compared to powders, therefore films are expected to exhibit slower gas adsorption kinetics than powders. In Chapter 4 it will be shown that a film may have smaller free volume elements near the surface than in the bulk.

Another possible cause of a decrease in porosity could be inadequate drying due to the increased difficulty of removing trapped residual solvent. It is also possible that, because the films are very thin (≤0.5 μm), cavities collapse more readily during the high vacuum degassing. If this is the case, then the loss of microporosity is not real but just an artefact of the analytical technique. Perhaps other methods like $^{129}$Xe-NMR or positron annihilation could be more useful in elucidating the microporous structure. Budd et al. reported larger N₂ BET surface area for powder than films.²⁷, ²⁸ Steiger et al. used PALS to investigate the effect of solvent on aging. Comparing freshly synthesised PIM-1 powder to a solution processed membrane, they found that the membrane has significantly large pores than the powder.²⁶ They thus inferred that the N₂ BET data suggests a great externally accessible surface area as opposed to the internal pore structure.
3.4.5 Effect of polymer structure on gas sorption behaviour

A number of structurally different microporous materials (PIM-1, TAPIM-1, PIM-2, PIM-1 CO1 copolymers series and the triptycene series) were used to investigate the influence of polymer structure on gas sorption behaviour.

3.4.5.1 Thioamide PIM-1 (TAPIM-1)

A comparison of the PSD for PIM-1 and TAPIM-1 (Figure 3.18) shows a reduction in microporosity on thioamide formation. This could possibly be due to the increased likelihood of the thioamide to facilitate the formation of intermolecular hydrogen bonding between the S group and amine hydrogen on adjacent polymer molecules (Figure 3.19). There is also the possibility of the existence of intra-molecular hydrogen bonding between the ether linkage and the amine hydrogen atoms. Intermolecular hydrogen bonding could possibly draw the molecules closer and reduce the sizes of the cavities that would contribute to the microporosity. Intermolecular hydrogen bonding would seal off some crevices and reduce the free volume of the polymer matrix. This networking could be responsible for the successive reduction of solubility of TAPIM-1 in chloroform or DMSO with time. Du et al.\textsuperscript{129} observed a decrease in O\textsubscript{2}, N\textsubscript{2}, He, H\textsubscript{2} and CO\textsubscript{2} permeabilities and increased pure-gas selectivities against N\textsubscript{2}. They noted that the presence of the carboxyl groups provide the conditions for carboxylated PIM-1 to exhibit inter and intra-molecular hydrogen bonding.

![Figure 3.18 Comparison of N\textsubscript{2} (77 K) PSD for PIM-1 (blue dots) and Thioamide PIM-1 (red triangles).](image-url)
Figure 3.19 Representation of probable intramolecular (red bonds) and intermolecular (blue bond) hydrogen bonding in TAPIM. The S group provides the electronegative site necessary for hydrogen bonding.

CO₂ adsorption (Figure 3.20) for the two materials is consistent with N₂ adsorption in that the TAPIM-1 isotherm is monotonically below that of PIM-1. This further lends more support to the observation that thionation results in a loss in free volume or microporosity. If considered per unit surface area, TAPIM-1 shows a higher uptake of CO₂ than PIM-1. This is evidence that TAPIM-1 preferentially interacts with CO₂, a characteristic that could make it useful in carbon capture applications.

Figure 3.20 Comparison of CO₂ (273 K) adsorption isotherms for PIM-1 (blue triangles) and TAPIM-1 (red diamonds)
3.4.5.2 PIM-2

Compared to PIM-1, PIM-2 would be expected to pack more efficiently owing to the rotation about the ‘biphenyl C-C bond’ as shown in Figure 3.21. Fluorine atoms are not bulky enough to restrict rotation and cause chirality. That being the case, then the polymer molecules will fold into each other and occupy space more economically thus effectively filling up cavities.

![Figure 3.21 90° Rotation about the ‘biphenyl C-C bond’ in PIM-2 causes more efficient packing and a decrease in microporosity.](image)

PIM-2 however, exhibits enhanced adsorption closer to $p/p^0 \sim 1$, this is evidence of a sharper transition to the bulk phase\(^{124}\) for N\(_2\) in PIM-2. This can be attributed to the condensation of N\(_2\) in the interstitial voids of the primary polymer particles.\(^4\) Similar behaviour has been observed in TripPIMs. Both isotherms exhibit pronounced hysteresis, which could be due to swelling\(^{130}\) of the polymer matrix. Furthermore, the N\(_2\) isotherms show the absence of mesoporosity, otherwise the desorption loop would be touching the adsorption loop around $p/p^0 = 0.4$.

A Horvath-Kawazoe treatment of the N\(_2\) adsorption data shows that the pore size distribution in PIM-2 remotely resembles that in PIM-1 as shown in Figure 3.22.
**Figure 3.22** $\text{N}_2$ (77 K) PSD for PIM-1 (blue triangles) and PIM-2 (red diamonds).

Notwithstanding the artificial nature of the peak around $0.6 - 0.7$ nm, useful comparisons can be based on the pattern displayed. Although the two distributions peak at roughly the same pore width, $\sim 0.65$ nm, PIM-1 exhibits more pores than PIM-2 for each pore width, so that the PSD for PIM-2 is constantly below that of PIM-1.
3.4.5.3 Ethano-anthracene PIM-1 copolymers

Figure 3.23 compares the N$_2$ (77 K) HK pore size distributions for the series of ethano-anthracene PIM-1 copolymers.

Figure 3.23 H-K Pore size distribution on PIM-1 co-polymers. PIM1-CO1-40 (blue diamonds), PIM1-CO1-50 (black squares), PIM1-CO1-61 (green dots), and PIM1-CO1-100 (red triangles).

At a glance it would appear the micropore analysis using the H-K method indicates a significant proportion of micropores with dimensions in the range 0.55-0.65 nm. But of course this is a simplistic explanation because these dimensions are very close to the performance limits of the technique, so that most likely any pore sizes below 0.55 nm are going to adsorb and show as a peak within the 0.55-0.65 nm range. The alternative approach would be to combine this data with pore size distribution data obtained from CO$_2$ adsorption as demonstrated with PIM-1 and PIM-7. Nevertheless, CO1-40 has the highest number of pores at size in that range. There is a cross-over around 0.6 nm between CO1-50 and CO1-100. These results are consistent with expectation. CO1-40 will be studied further in Chapter 4 with respect to N$_2$ and Xe sorption.

The pore size distribution is strongly biased towards pores in the range 0.55-0.65, indicating the co-polymers are predominantly microporous. As with the monomers in PIMs, it seems possible to tune the pore size distribution in these co-polymers by careful choice and proportion of co-monomers. To this extent, these materials are comparable to PIM-1 and triptycenes.$^{62}$
The monomer 9,10-dimethyl-9,10-dihydro-9,10-ethanoanthracene-2,3,6,7-tetrol, which is added in increasing amounts to the spiro unit, has a roof-like structure (Figure 3.24) prescribed by the ethano bridge above the middle ring. It provides an additional kink into the PIM-1 structure resulting in less dense packaging of the polymer chains that should result in a higher free volume.

**Figure 3.24** The structure of the CO1 spiro-unit in PIM-1 co-polymers. The ethano bridge introduces an extra kink in the PIM-1 structure resulting in increased microporosity.

A more revealing evaluation of the effects of introducing the CO1 co-monomer into the PIM-1 structure can be carried out by measuring pore sizes of the materials using different methods. Chapter 4 addresses this by studying PIM1-CO1-40 and PIM-1.
3.4.5.4 Triptycene based PIMs (TripPIMs)

(a) Hydrogen sorption at 77 K by triptycene based PIMs

Figure 3.25 shows the H$_2$ PSD for the different triptycene networks. Shorter or branched chains provide triptycene based PIMs of higher BET surface area (section 2.5.2) and greater microporosity, while longer chains apparently block the microporosity created by the rigid polymer structure. Overall, the Triptycene based PIMs have a high population of micropores of subnanometer proportions. Compared to non-network PIMs, triptycenes generally have a higher microporosity except for those possessing long (R = Pe, Oct) and bulky (R = Bz) alkyl chains.

![Figure 3.25 H$_2$ (77 K) HK pore size distribution for TripPIMs. HTripPIM (blue diamonds), MeTripPIM (red triangles), EtTripPIM (black triangles), n-PrTripPIM (green crosses), i-PrTripPIM (purple stars), n-BuTripPIM (brown dots), i-BuTripPIM (brown circles), PeTripPIM (blue dashed line), OctTripPIM (blank triangles), BzTripPIM (pinkish diamonds).](image)

It therefore is apparent that the microporosity and gas adsorption of these materials can be tuned by choice of the length and branching of the two alkyl chains at the 9, 10- position of the triptycene subunits. By implication, this allows tuning of BET surface area in the range: 600 – 1760 m$^2$ g$^{-1}$. The MeTripPIM homologue was studied in more detail.
(b) MeTripPIM

From the N$_2$ adsorption data (Figure 3.26) the BET surface area for MeTrip-PIM is 1760 m$^2$ g$^{-1}$. This is higher than reported for other PIMs.\textsuperscript{9, 27, 39} The adsorption isotherm exhibits distinct hysteresis stretching to low partial pressures between the adsorption and desorption loops. This could possibly be a result of activated adsorption due to either a swelling of the polymer matrix or from the limited access of nitrogen molecules to pores due to constrictions at narrow apertures.\textsuperscript{32, 78}

![Figure 3.26 N$_2$ (77 K) adsorption (bold diamonds) and desorption (blank diamonds) isotherms for MeTripPIM.](image)

Figure 3.26 shows the CO$_2$ adsorption isotherm at 273 K for MeTripPIM.
The Horvath-Kawazoe analysis of the low-pressure nitrogen adsorption data shows that the pore size distribution within MeTripPIM is severely skewed towards sub-nanometre pores (Figure 3.28). The triptycene component serves to provide the nonlinearity necessary for microporosity, a function played by the spirocentre in PIM-1, PIM-2, or PIM-7. This also facilitates polymer growth in the same plane with the exposed faces of the ribbon-like protrusions, between the branching triptycenes, aligned at right angles to the plane of the polymer. The efficient hindrance of close, face-to-face association between these fused-ring struts helps limit space-efficient packing of the macromolecules further, causing enhanced microporosity.

The N\textsubscript{2} and CO\textsubscript{2} data in Figures 3.26 and 3.27 have been converted to pore size distributions using the Horvath-Kawazoe method. It appears that the modal pore size is ca. 0.78 nm, directly above the point where the two distributions overlap. This makes MeTripPIM a microporous material as defined by IUPAC.\textsuperscript{66}
Figure 3.28 CO$_2$ (red dots, 273 K) and N$_2$ (blue squares, 77 K) pore size distributions for MeTripPIM
3.5 Conclusions

In view of the preceding results, the following deductions can be made:

The sorption methodology was validated. There was agreement between BET surface area values obtained from the in-house comparison of the Coulter 3100 and the ASAP 2020. A significant discrepancy however, was observed when these were compared against an external laboratory using the Coulter 3200. An attempt was made to understand and explain this difference and an adjustment to the outgas protocol on the ASAP 2020 proposed. The ASAP 2020 ‘over-degasses’ the sample and consequently causes collapse of the microporous structure. A ‘mild’ degas regime that uses a lower temperature (70 °C) and a shorter degas period (8 h) was proposed.

The use of N\textsubscript{2} to characterise microporosity at pore widths below 0.7 nm using a turbo-molecular pump equipped instrument is not recommended because the highest vacuum reached (~10\textsuperscript{-8} bar) does not allow N\textsubscript{2} to characterise pores below this width despite accessing them.

The HK PSD agrees reasonably well with data from other methodologies or techniques like crystallography. While to this extent it is widely useful, it would be unreasonable to expect the HK model to account for every contingency. Although the HK model has inherent flaws due to its assumptions, and despite being limited by the estimation of physical properties like the density conversion factor, the number of molecules of adsorbate per unit area of adsorbent surface (\(N_s\)), and in some cases the estimation of saturation pressure (\(p^0\)), it still provides a scientifically adequate account of the pore size distribution in the microporous materials under study.

The Dubinin-Astakhov model overestimates the average pore width of the microporous materials under study, and is therefore not suitable for the characterisation of such materials.

The DFT approach generates data that oscillated between positive and negative pore volumes, which does not give much information on the micropores. However, when the negative values are ignored the positive values over-estimate the pore widths.
The BJH model also overestimates pore widths and is thus unsuitable for the characterisation of Microporous materials.

CO₂ at 303 K is an adsorptive that behaves similarly to N₂ at 77 K at \( \frac{p}{p^0} \geq 0.8 \). Thus it is a convenient technique to complement N₂ adsorption at 77 K.

Despite the inherent error in estimating the density of CO₂ at 303 K as incorporated into the density conversion factor, CO₂ at a higher pressure is more useful than at 273 K \(^\text{(101)}\) although combining PSD data for CO₂ at 273 K with that for N₂ at 77 K gives the overall porosity characterisation of microporous materials like PIMs.

Some of the physical properties of the probe gases (CO₂, H₂ and N₂) were estimated from data available from literature, and will consequently limit the accuracy of the resultant PSD. The general trend however, remains significant as it gives an insight into the microporosity of the materials under study and also allows a consistent comparison between different materials.

Use of the Ross-Olivier parameter (which uses a lower value of the magnetic susceptibility for C : 1.05 \( \times 10^{-29} \), instead of the 1.35 \( \times 10^{-28} \) used in the original HK method. This effectively lowers the interaction parameter) underestimates the pore widths. Using the Ross-Olivier parameter with cylindrical geometry (Saito-Foley) however, gave results comparable to the HK model with slit pore geometry.

PIM-1 is a highly microporous polymer. Its uptake of gas is however, significantly reduced upon forming a film. This could be because of the trapped solvent which is more difficult to remove even by drying in a vacuum oven. Consequently the surface layer of the film is denser, thus gas sorption is mitigated by slow kinetics. Yampolskii et al. found that residual chloroform from film casting significantly reduces membrane permeability.\(^\text{(131)}\) The interaction of PIM-1 with solvent is explored further in Chapter 5. Clearly then, the sample form alters the sorption properties of the material as exemplified by PIM-1.

The structure of a polymer material significantly affects its gas sorption properties. Modifying the nitriles on PIM-1 into amines and introducing an S group effectively reduced the microporosity of the polymer, thus altering the properties
of PIM-1. The electronegativity introduced by the sulphur group was thought to have caused inter and intra-molecular hydrogen bonding.

While the PIM-2 synthesised in this research is less microporous than PIM-1, it has significantly high free volume all the same. The free rotation about the biphenyl C-C bond causes more efficient packing than in PIM-1 where there is no rotation.

Triptycene based PIMs have enhanced microporosity due to the macromolecular shape of the framework which reduces rotation and frustrates efficient packing.
Chapter 4: Free Volume and Ageing of PIM-1 and Ethanoanthracene PIM-1 Copolymers
Chapter 4: Free Volume and Ageing of PIM-1 and PIM-1 Ethano-anthracene Copolymers

4.0 Introduction

This chapter investigates free volume properties of a PIM-1 copolymer (PIM-CO1-40) and compares it against PIM-1. The effect this has on ageing of the polymer in membrane and powder forms is explored. A number of independent techniques, namely $N_2$ sorption, $Xe$ sorption, Positron annihilation lifetime spectroscopy (PALS) and $^{129}Xe$ NMR are used to probe the free volume. $N_2$ sorption measurements and analysis of $N_2$ and $Xe$ sorption data were undertaken in Manchester. The copolymer was synthesised and $Xe$ sorption and $^{129}Xe$ NMR measurements were performed at Helmholtz-Zentrum Geesthacht (formerly GKSS Research Centre), Germany (Thomas Emmler, Kathleen Heinrich and Detlev Fritsch). PALS was performed at Universität Kiel, Germany (S. Harms, Klaus Ratzke, and Franz Faupel), and at Universität der Bundeswehr München, Neubiberg and FRM II TU München (W. Egger and L. Ravelli).

4.1 Free volume

The free volume of a polymer material is that space left unoccupied by its molecules. An amorphous material contains hole free volume in addition to interstitial free volume. This generally accounts for about 10 % decrease in density in the amorphous state relative to the crystalline state. Hole free volume (FVH), which is a consequence of disordered, static or dynamic, molecular packing, exists as many irregularly shaped free volume elements called holes. The occupied space is a function of the specific volume of the polymer, $V$ and van der Waals volume, $V_w$ as indicated in Equation 4.1.

$$f_v = \frac{V - 1.3V_w}{V}$$  \hspace{1cm} (4.1)

Excess free volume, $f_v$, can be trapped into a polymer if it is quenched from a rubbery to a glassy state. The delayed relaxation of polymers above the glass transition temperature can cause retention in local inhomogeneities. Such inhomogeneities can disappear during repeated temperature measurement cycles.
Sorption of Gases and Liquids by Polymers of Intrinsic Microporosity (PIMs)

FVH are important since they determine the polymer’s properties, namely elasticity, deformability, permeability, selectivity and ageing.

4.2 Physical Ageing

Free volume may be lost gradually with time in a process called physical ageing. This is accompanied by a decrease in diffusivity. Physical ageing of a polymer membrane is therefore effectively the decrease in the free volume of the polymer (while in operation or storage). This in turn affects the transport properties, and hence the application of glassy polymer membranes. The key properties of membranes are gas solubility \( S \), diffusivity \( D \), permeability \( P \), and gas selectivity \( \alpha \) and are related as shown in Equation 4.2 (a) and (b).

\[
P = SD \tag{a}
\]

\[
\alpha = \frac{P_A}{P_B} = \frac{S_A D_A}{S_B D_B} \tag{b}
\]

Selectivity compares the relative permeabilities of two molecules, \( A \) and \( B \) for example. High free volume and well developed microporosity are necessary for high membrane permeability.

It has been reported that the type of solvent regime involved in the membrane casting protocol affects the physical properties and hence the ageing of a polymer membrane.

4.3 PIM-1 copolymers incorporating the ethano-anthracene unit

The synthesis and structure of PIM-1 copolymers were presented in Chapter 2. This chapter focuses on PIM1-CO1-40 (spiro-units: CO1 = 60:40) sorption properties and free volume in comparison to PIM-1. A number of different techniques, namely \( N_2 \) sorption, Xe sorption, \(^{129}\)Xe NMR and PALS, were used to characterise this free volume. \(^{129}\)Xe NMR and PALS are sensitive for the local structures, and \( N_2 \) and Xe sorption will provide a more integrated view into the material. A brief overview of these techniques is presented next.
4.4 Analytical approaches

4.4.1 N₂ and Xe sorption

N₂ sorption and Xe sorption are usually used when determining the free volume and pore sizes of porous materials. Because a xenon atom is much larger than a nitrogen molecule, the surface and pore sizes they probe are different.

4.4.2 ¹²⁹Xe NMR

¹²⁹Xe NMR spectroscopy has proven to be a valuable tool for the determination of pore sizes in inorganic materials like, e.g., zeolites and polymers, including high free volume polymers such as Teflon AF-types.

The sorption behaviour of Xe in relaxed PIM-1 and PIM1-CO1-40 can be described using the dual sorption model. Suzuki¹³⁵, ¹³⁶ developed a method for calculating the hole sizes in glassy polymers and polymer blends using the Xe chemical shifts.⁴, ¹³⁵, ¹³⁶ The observed chemical shift, \( \delta_{\text{obs}} \), is determined by the Xe wall interactions \( \delta(S) \), the Xe-Xe interactions \( \delta(Xe) \), the residual interactions, \( \delta(E) \) for the electric field due to cations, \( \delta(SAS) \) for the shift in strong absorption places, and \( \delta(M) \) for the contribution of magnetic compensation cations (Equation 4.3).

\[
\delta_{\text{obs}} = \delta(S) + \delta(Xe) + \delta(E) + \delta(SAS) + \delta(M)
\]  

(Equation 4.3)

The last three terms have no significance for organic polymers like PIM-1 and PIM1-CO1-40. Thus according to this approach, sorption sites are divided into Langmuir and Henry adsorption. Assuming the chemical shift results from fast exchange between Langmuir and Henry sites, it is possible to recalculate the chemical shifts (\( \delta_D \) and \( \delta_H \)) that characterise them as shown in Equations 4.4 and 4.5.

\[
\delta_D = \delta(Xe)_D + \delta(S)_D
\]  

(Equation 4.4)

\[
\delta_H = \delta(Xe)_H + \delta(S)_H
\]  

(Equation 4.5)
Knowing the relative amounts ($\phi_D$ and $\phi_H$, $\phi_D + \phi_H = 1$) in these sites, Equation 4.6 can be used.

$$\delta_{obs} = \phi_D \delta_D + \phi_H \delta_H$$  \hspace{1cm} (4.6)

From a plot of pressure against chemical shift, an extrapolation to zero pressure gives the ‘pure’ chemical shift of Xe wall interaction and permits the calculation of the mean hole sizes of the polymer that is accessed by a Xe atom (Equation 4.7).

$$\lambda = \frac{243 \times 2.054}{\delta(S)_H} - 2.054 = \frac{D_S - D_{Xe}}{2}$$  \hspace{1cm} (4.7)

It is therefore possible to calculate the mean free path of a Xe atom together with the diameter for a spherical hole using a Xe atom diameter ($D_{Xe}$) of 0.437 nm as given in Table 4.1.

### 4.4.3 PALS

PALS is one of the most suitable experimental techniques to characterize the hole free volume in amorphous polymers and low molecular weight organic materials. In this technique, positronium in its ortho-state, $\sigma$-Ps, is used as a probe for local free volume holes. After being injected from a radioactive source, positrons form a bound, hydrogen-like positron-electron system called positronium, Ps. Positroniums tend to be localised in holes, and the hole size determine the annihilation lifetimes of long-lived orthopositronium. Thus the technique is basically the measurement of the lifetime of the orthopositronium. The lifetime of orthopositronium states, $\tau_{\sigma-Ps}$ can be correlated to the free volume hole sizes in polymers.$^{137, 138}$

A quantum mechanical model for calculating free volume hole sizes that assumes a positronium particle to be confined in a sphere and potential well of infinite wall height was developed by Tao et al.$^{137, 139}$ The model further postulates interaction between an orthopositronium and an electron layer at the pore wall. This evokes use of the Schrodinger equation. The relationship between positronium lifetime and the hole radius is obtained from calculation of the overlap integral of the positronium probability density function with the electron layer (Equation 4.8).
\[
\tau_{o-\mu} = \frac{\lambda^0}{\tau} \left( 1 - \frac{R_h}{R_h + \delta R} + \frac{1}{2\pi} \sin \frac{2\pi R_h}{R_h + \delta R} \right)
\]  

(4.8)

Where

- \( \tau_{o-\mu} \) is the reciprocal of the orthopositronium decay rate,
- \( \lambda^0 \) is the spin averaged decay rate in the electron layer
- \( R_h \) is the hole radius
- \( \delta R \) is the thickness of the electron layer.

Hole sizes in amorphous polymers have a broad distribution, therefore the hole size obtained from PALS is regarded as an average. This technique is very useful in obtaining detailed free volume characteristics of a polymer, and it can also generate dynamic molecular simulation data. However, it can be limited by the rather short lifetimes associated with amorphous polymers. This makes small differences in orthopositronium lifetimes in structurally different regions indistinguishable.

PALS and \(^{129}\text{Xe} \) NMR give information about the average microscopic size of free volume entities\(^{137}\). Used together, these techniques should shed more light on the relationship between structure and properties of high free volume materials.
4.5 Experimental

4.5.1 N₂ Sorption

PIM-1 (batch number CT/02/07) was synthesised as described in Chapter 2. N₂ sorption measurements at 77 K were performed as described in Chapter 2, and the subsequent data treatment to convert isotherms to pore size distributions was carried out using the Horvath-Kawazoe model (Equation 3.32) as described in Chapter 3.

4.5.2 Xe Sorption

Xe sorption was measured for the same pressure range as for the ¹²⁹Xe NMR experiments using magnetic suspension balances from Rubotherm. A glass version was applied for measurements up to 1.5 bar, and a metal version up to 3 bar of Xe pressure. The samples (300 mg PIM-1 and 100 mg PIM1-CO1-40) were sealed into a polyphenylenesulfide (PPS) fleece and dried at 120 °C in an oil-free high vacuum for at least 12 h to desorb any potential condensable contaminants. No significant sorption for the PPS fleece to Xe was detected. After transfer into the magnetic scale the samples were dried again overnight in an oil-free high vacuum. After 15 minutes there was no further mass change after setting the Xe pressure, starting from high vacuum. Measurements were performed at 298 K.

4.5.2.1 Manipulation of Xe sorption data

In order to calculate the interaction parameter for Xe, \( N_m \) has to be obtained first (Figure 4.1). The technique used to estimate the number of Xe atoms per unit area of surface covered is similar to that used for H₂ in Chapter 3.
Figure 4.1 Estimation of $N_m$ for Xe using the Free energy of adsorption plot.

Table 4.1 Physical properties for calculating PSD from Xe sorption measurements.

<table>
<thead>
<tr>
<th>Physical property</th>
<th>Xe (298 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter (nm)</td>
<td>0.437</td>
</tr>
<tr>
<td>Polarisability (cm$^3$)</td>
<td>4.00x10$^{-24}$</td>
</tr>
<tr>
<td>Magnetic Susceptibility (cm$^3$)</td>
<td>7.04x10$^{-29}$</td>
</tr>
<tr>
<td>No. of atoms per unit area of surface (molec. cm$^{-2}$)</td>
<td>*5.30x10$^{14}$</td>
</tr>
<tr>
<td>Density conversion factor</td>
<td>**0.0043378</td>
</tr>
</tbody>
</table>

* obtained by calculation using the BET, DR and B-point surface areas on a microporous silver adsorbent$^{124}$. **this is at 289 K.

To calculate pore size distributions, an algorithm similar to that for CO$_2$ at 303 K (Chapter 3) was performed as follows:
1. $\sigma$ was calculated as described by Everett and Powl.\textsuperscript{107}
2. Horvath-Kawazoe constants were then calculated using Equations 3.31.
3. Pore widths ($L - d_p$) were calculated for given $p/p^0$ values.

4. $p/p^0$ values were taken from the range $0 \leq p \leq 3500$ mbar using $p^0 = 70775.72$ mbar, obtained by extrapolating temperature versus vapour pressure (Patterson et al.\textsuperscript{140}).
5. Pore width values were inferred from $p/p^0$ values tabulated in step 3.
6. The volume of Xe adsorbed ($V_{ads}$) was calculated from $V_{ads} = Q_{ads} \times 22414/Ar$, where $Q_{ads}$ is the quantity adsorbed in mmol g$^{-1}$.
7. The cumulative volume adsorbed ($V_{cum}$) was calculated from $V_{cum} = V_{ads} \times \rho_{CF}$. A value of the density conversion factor ($\rho_{CF}$) at 289 K was used (no data for 298 K).

Using the HK equation, these values were used to convert Xe isotherm data to pore size distributions.

4.5.3 $^{129}$Xe NMR

For $^{129}$Xe NMR the samples were placed in pressure-stable NMR tubes. Prior to the NMR experiments, the samples were heated to 120 °C at oil-free high vacuum for at least 12 h to remove any adsorbed vapours. For sample preparation, the sample-filled NMR tube was annexed to a vacuum/pressure line fitted with an adjustable cooling/warming bath for the sample tube that allowed control of the Xe pressure over the sample from 0 to about 3 bar at the given temperature. Xenon then was applied. After equilibrium sorption of Xe, indicated by stable Xe gas pressure for at least 15 minutes, the sample was quickly transferred into the NMR magnet and a further 15 minutes was allowed for temperature equilibration. All $^{129}$Xe NMR experiments were performed on a Bruker Avance NMR Spectrometer operating at a field of 7 T (83.03 MHz for $^{129}$Xe). The spectra were recorded applying 30 pulses (5 $\mu$s); the repetition time was chosen in such a way that the sample was fully relaxed.
4.5.4 Positron Annihilation Lifetime Spectroscopy (PALS)

4.5.4.1 Preparation of thin films

Thin films of PIM-1 (batches CT/02/07 and GP35) (0.3 μm) were made by spin-coating a PIM-1 solution in chloroform onto 2 cm² silica wafers and their thickness measured as described in section 2.4.5.1. The thick film (3.8 μm) was prepared by solvent evaporation as described in section 2.4.5.2. Table 4.2 shows the film thicknesses and details of how they were prepared.

Table 4.2 Preparation of PIM-1 films by spin-coating onto silica wafers and solvent evaporation

<table>
<thead>
<tr>
<th>Film thickness (μm)</th>
<th>Preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>Cast from PIM-1 batch CT/02/07 in chloroform (20 mg cm⁻³). Spin-coated at 1000 rpm for 1 minute. Soaked in methanol for 24 h before being dried in a vacuum oven at 70 °C for 4 h to remove residual solvent.</td>
</tr>
<tr>
<td>1.3</td>
<td>Cast from PIM-1 batch CT/02/07 in chloroform (40 mg cm⁻³). Spin-coated at 500 rpm for 1 minute. Residual solvent removed as above.</td>
</tr>
<tr>
<td>3.8</td>
<td>Cast by solvent evaporation from PIM-1 batch CT/02/07 (20 mg cm⁻³). Solvent was evaporated at room temperature in a glass petri dish covered with a lid to regulate the rate of solvent evaporation. Methanol treatment and vacuum drying to remove residual solvent was performed as above.</td>
</tr>
</tbody>
</table>
4.5.4.2 PALS measurement on PIM-1 films

The age of the PIM films was 293 days at the time of the experiment. Experimental conditions for the PALS experiment were: vacuum: $10^{-7}$ mbar; spot size: 4 mm$^2$, counting rate: 5500 cts/s, total counts per spectrum: 4 million, measurement time per spectrum: 12 min; 3 - 7 energy steps, total measurement time per sample: 1 - 2 hours. Spectra were converted to the data format and evaluated with LT 9, a program which takes into account the distribution in free volume assuming a log-normal distribution in o-Ps lifetime.
4.6 Results and Discussion

4.6.1 \( \text{N}_2 \) Sorption

From \( \text{N}_2 \) sorption measurements, the BET surface areas of PIM-1 and PIM1-CO1-40 are 720 and 760 m\(^2\) g\(^{-1}\) respectively. Figure 4.2 compares the \( \text{N}_2 \) sorption isotherms at 77 K for these materials. As expected of microporous materials, both polymers exhibit high gas uptake at low relative pressures. In addition, they both show hysteresis, a phenomenon associated with swelling effects.

![Figure 4.2 N\(_2\) (77 K) isotherms for PIM-1 (black squares), and PIM1-CO1-40 (red circles). Bold symbols stand for adsorption, and blank symbols stand for desorption](image.png)

Use of the HK model to analyse very low relative pressure regions of the adsorption isotherms gives the pore size distribution shown in Figure 4.3. Both materials show a broad distribution of effective pore size in the micropore region. As alluded to before in Chapter 3, the apparent peak at ~0.6 nm represents the lowest experimentally achievable pressure with a turbomolecular pump and includes a contribution from smaller pores. The significant difference between these polymers is that PIM-1 exhibits a lower \( \text{N}_2 \) uptake over a pressure range corresponding to 0.65 – 0.7 nm. This seems to be the ‘missing’ porosity in this
pore size range that leads to a lower total uptake of N\textsubscript{2} and a lower BET surface area. This will be revisited in the scope of Xe sorption.

![Figure 4.3 N\textsubscript{2} (77 K) PSD for PIM-1 (black squares) and PIM1-CO1-40 (red dots)](image)

**4.6.2 Xe Sorption**

In order to record the history of the sample and investigate its bearing on any ageing effects, the order in which Xe sorption measurements were done is shown in Table 4.3.

**Table 4.3 Order of Xe Sorption Measurements**

<table>
<thead>
<tr>
<th>Run number</th>
<th>Sorption Temperature (( ^\circ)C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PIM-1</td>
</tr>
<tr>
<td>1</td>
<td>85</td>
</tr>
<tr>
<td>2</td>
<td>25</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
</tr>
<tr>
<td>4</td>
<td>25</td>
</tr>
<tr>
<td>5</td>
<td>25</td>
</tr>
</tbody>
</table>

For PIM-1, the sorption loops at 85 \( ^\circ\)C (Run 1), and more so at 25 \( ^\circ\)C (Run 2), showed an unexpected inflection in the pressure range 10 – 1 500 mbar (Figure
4.4). PIM1-CO1-40 showed non-ideal Xe uptake in the region below 100 mbar at 85 °C (Figure 4.5). Adsorption at 100 °C followed this unexpected behaviour up to 3 bar. A re-run at 25 °C (Run 4) showed expected behaviour for both polymers. To check the ageing effect of Xe adsorption at 100 °C, the PIM-1 sample was redissolved in chloroform, precipitated in methanol and dried at 80 °C for at least 10 hours followed by more drying at 120 °C under high vacuum for 12 hours before Xe sorption measurement at 25 °C (Run 5). This resulted in recovering the inflection in Xe uptake, albeit to a lesser degree. This seems to suggest that precipitation of PIM-1 kinetically traps an ‘unrelaxed’ structure. Sorption at 100 °C possibly plasticises the material sufficiently to relax it.

![Figure 4.4 Xe Sorption on PIM-1 at the 1st to 5th cycle and after redissolving in chloroform and reprecipitated in methanol (Run 5).](Data courtesy of Thomas Emmler, Kathleen Heinrich and Detlev Fritsch)
Sorption of Gases and Liquids by Polymers of Intrinsic Microporosity (PIMs)

Figure 4.5 Xe sorption on PIM1-CO1-40 at the 1st to 4th cycle. (a) the full isotherms, (b) a blow up of the low pressure region. (Data courtesy of Thomas Emmler, Kathleen Heinrich and Detlev Fritsch)

As in the case of low pressure N\textsubscript{2} adsorption, the HK model can be applied to low pressure Xe adsorption data (Figure 4.5 b) to generate a pore size distribution. To achieve this, the physical constants quoted in Table 4.1 were used. Applying the HK model to Xe sorption data at 25 °C for PIM1-CO1-40 and for both ‘unrelaxed’ and ‘relaxed’ PIM-1 samples results in the pore size distributions shown in Figure 4.6. Consistent with N\textsubscript{2} sorption data, the copolymer PSD shows a broad distribution of pore sizes in the range 0.6 – 1 nm. Relative to ‘relaxed’ PIM-1, there appears to be ‘missing’ porosity in ‘unrelaxed’ PIM-1 in the pore size range 0.55 – 0.7 nm. This is in agreement with the observations on N\textsubscript{2} adsorption data. ‘Missing’ porosity in a material could be due to kinetically trapping larger voids on precipitation which subdivide as the polymer relaxes, or because there are dense regions that open up upon relaxation. It appears from Figure 4.6 that PIM1-CO1-
40 has pore sizes shifted to larger values than ‘relaxed’ PIM-1. This could possibly be ascribed to the reduced torsional flexibility of the ethanoanthracene unit in the copolymer as compared to the spiro-unit in PIM-1.

Figure 4.6 Xe (298 K) PSD using the HK model for PIM-1 and PIM1-CO1-40. The bold square show PIM-1 before Xe adsorption at 373 K, and blank squares show PIM-1 after Xe adsorption at 373 K (Table 4.3)

4.6.3 $^{129}$Xe NMR

$^{129}$Xe NMR at various pressures was used to investigate free volume in PIM-1 and PIM1-CO1-40 polymers. The sequence of measurement of the samples is given in Table 4.4.

Table 4.4 Sequence of $^{129}$Xe NMR measurements

<table>
<thead>
<tr>
<th>Run Number</th>
<th>Temperature ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>-25</td>
</tr>
<tr>
<td>4</td>
<td>25</td>
</tr>
</tbody>
</table>

For run 1, whereas PIM-1 shows two distinct linear regions separated by a plateau in the $^{129}$Xe chemical shift versus pressure plot, PIM1-CO1-40 exhibits a monotonic rise in chemical shift with pressure (Figure 4.7).
Figure 4.7 Comparison of the pressure dependent $^{129}$Xe chemical shift at 25 °C for run 1. (Data courtesy of Thomas Emmler, Kathleen Heinrich and Detlev Fritsch)

Subsequent measurement (runs 3 and 4) to the 100 °C measurement at 3 bar Xe pressure resulted in ‘normal’ spectra (Figure 4.8). This is consistent with Xe sorption measurements as discussed earlier.

Figure 4.8 Comparison of the first $^{129}$Xe NMR measurement at 298 K (red squares), and the measurement at 298 K after conditioning (green squares) (Data courtesy of Thomas Emmler, Kathleen Heinrich and Detlev Fritsch)
Treatment of the polymers at 100 °C and 3 bar relaxes and conditions the polymer and its free volume structure. As observed earlier, N₂ and Xe sorption data suggest decreased accessible porosity in the range 0.6 – 0.7 nm for ‘unrelaxed’ PIM-1 compared to the ‘relaxed’ material. At 25 °C and 1 bar, pores of width 0.75 nm and below are filled with Xe. Extrapolating the NMR data in this region gives a higher chemical shift for ‘unrelaxed’ PIM-1, which corresponds to a smaller pore size when compared to ‘relaxed’ PIM-1 or PIM1-CO1-40. Above 2 bar pores of effective width ≤ 0.84 are filled, and the NMR data also give a larger effective pore size.

A summary of hole diameters obtained by ¹²⁹Xe NMR is presented in Table 4.5.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Temperature (°C)</th>
<th>Diameter of spherical hole (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PIM-1</td>
<td>25</td>
<td>1.0–1.07</td>
</tr>
<tr>
<td>PIM-1</td>
<td>100</td>
<td>0.82–0.90</td>
</tr>
<tr>
<td>PIM1-CO1-40</td>
<td>25</td>
<td>0.88–0.96</td>
</tr>
</tbody>
</table>

### 4.6.4 Ageing of PIM-1

#### 4.6.4.1 Investigation of ageing using PALS

The date of film preparation was 27/05/2009, and the PALS measurements were performed on 09/2009 (after 118 days) and 17/03/2010 (after 293 days).

As shown in Figure 4.9, the intensity, $I_3$ being a measure of o-Ps formation probability and hole concentration, does not depend on storage time, but rather varies in a characteristic manner with implantation energy, $E$.

The o-Ps lifetime, $\tau_3$ measures the free volume. For the thick film (3.8 μm), $\tau_3$ decreases with increasing storage time whereas for the thin film (0.3 μm) a saturation level is attained. This is more pronounced at high implantation energies, reflecting high penetration depth. The orthopositronium lifetime decreases with decreasing acceleration voltage. This implies the average hole size is smaller for smaller penetration depths thus indicating a gradient of free volume.
Figure 4.9 O-Ps lifetime $\tau_3$ (squares) as a measure of free volume and Intensity $I_3$ (circles) for three different polymer films as function of implantation energy, $E$. Filled symbols are results from the measurement after 293 days, open symbols are results from measurements after 118 days. Red symbols are for 0.3 $\mu$m, green symbols are for 1.3 $\mu$m, and orange symbols are for 3.8 $\mu$m films. (Data courtesy of S. Harms, K. Ratzke, W. Egger and L. Ravelli).

The ageing of PIM-1 films and reduction in free volume can therefore, be followed by PALS with a moderated beam.

4.6.4.2 Investigation of ageing of PIM-1 by monitoring the BET surface area and pore volume

$N_2$ sorption measurements were performed on PIM-1 samples (batch CT/02/07) prepared in March 2006, using the procedure outlined in Chapter 2, over a period of time. The variation of the BET surface area and the pore volume at $p/p^0 \sim 0.05$ at the different times is shown in Table 4.6. The BET surface area decreases
monotonically with time. Staiger et al.\textsuperscript{26} showed that permeability decrease linearly with time.
Table 4.6 The variation of BET surface area and pore volume (at $p/p^0 \sim 0.05$) for PIM-1 powder over time

<table>
<thead>
<tr>
<th>Measurement</th>
<th>BET surface area (m$^2$ g$^{-1}$)</th>
<th>Pore volume at $p/p^0 \sim 0.05$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>790</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>720</td>
<td>0.26</td>
</tr>
<tr>
<td>3</td>
<td>693</td>
<td>0.25</td>
</tr>
<tr>
<td>4</td>
<td>698</td>
<td>0.24</td>
</tr>
<tr>
<td>5</td>
<td>650</td>
<td>0.23</td>
</tr>
</tbody>
</table>

Measurement 1 was run in March 2006, measurement 2 in July 2008, measurements 3 and 4 in May 2009 (the BET surface areas for these measurements are not significantly different), and measurement 5 in June 2009.

BET surface area does not necessarily imply high microporosity. To investigate the effect of ageing on free volume, a comparison of the pore volumes as seen by the N$_2$ probe at $p/p^0 \sim 0.05$ was made. This relative pressure, which represents a HK pore width of 1.30 nm, only serves as a reference point at which comparisons can be made. Like the BET surface area, the pore volume decreases with time. Taking pore volume accessible to N$_2$ as an indicator of the free volume generally accessible to penetrants, the gradual loss of pore volume with time would mean a general decrease in the capacity of the polymer to adsorb guest molecules with time. This however cannot be readily generalised for membranes since the dissolution and casting process should be independent of the polymer history. Nevertheless, used in the powder form aged material is likely to have diminished gas permeation capabilities. As observed in N$_2$ and Xe sorption measurements before, methanol treatment or some other thermal and pressure regime should restore the microporosity.
4.7 Conclusion

An extensive study of PIM1-CO1-40, a copolymer with a 60:40 ratio of spiro-units to CO1 units, was undertaken and compared with PIM-1. All the methods used, namely N$_2$ sorption, Xe sorption, $^{129}$Xe NMR and PALS, show that these polymers are microporous. In comparison with the copolymer, the PIM-1 batch studied shows anomalous $^{129}$Xe NMR, N$_2$ and Xe sorption behaviour, which could be due to reduced porosity in the pore size range 0.6 – 0.7 nm. Upon conditioning and relaxing the polymer, the anomalous behaviour was removed. Unlike PIM-1, the copolymer did not show effects of Xe conditioning under these conditions.

The distribution of free volume, and hence the sorption and transport properties in the materials studied, has been shown to depend on the history of the sample. Suitable treatment such as with Xe at 100 °C and 3 bar, or soaking in methanol for 24 h, results in the relaxation of the polymer and its free volume structure.

PALS measurements on PIM-1 films, and N$_2$ sorption measurements on PIM-1 powder showed that PIM-1 gradually lost its porosity with time. Free volume of glassy polymers, and by implication permeation and sorption properties, are time-dependent and are reduced after prolonged storage and operation time.
Chapter 5: Interaction of PIMs with penetrants
Chapter 5: Interaction of PIMs with penetrants

5.0 Overview

The chapter begins by discussing how guest molecules in the liquid phase, especially residual solvent from membrane casting and alcohols from residual solvent removal, interact with the PIM-1 polymer matrix. An abridged historical background and the structure of the hydrogen bond (HB) are then presented. A brief treatment of how selected techniques can be used to characterise the HB is given and ATR-FT-IR presented as the method of choice. The possible sites of interaction are explored and frequency shifts in ATR-FT-IR spectra used to identify them and compare relative strengths of the HB.

5.1 Introduction

Traditionally, removal of dissolved organics from aqueous systems has been achieved through the use of activated carbons. Maffei et al. demonstrated that a phthalocyanine network PIM has a high affinity for phenol, 4-nitrophenol, orange II, and naphthol green B, and thus can be used to selectively remove these from aqueous solution. PIM-1 has also been reported to have a high selectivity for organics, it therefore could be used for similar or related purposes. For it to be useful for a wider range of applications, PIM-1 has to be solution processed into membranes. However, there is an influence of material processing on porosity. During the synthesis stage, precipitation from strongly interacting solvents like DMF or DMAc tend to reduce microporosity, whereas solvents like chloroform enhance the porosity. Impregnation of polymer membrane with solvents like methanol before removing them in a vacuum oven should exclude pore blocking by trapped solvents. Thus sorption and permeation properties will depend upon the film preparation protocol. Budd et al. showed that impregnating PIM-1 films with alcohols like methanol or ethanol enhances the film permeability, whereas water decreases it (Table 5.1).

Table 5.1 Gas Permeation Parameters (Determined by the Gas Chromatographic Method) of PIM-1 Films after Different Pretreatments

<table>
<thead>
<tr>
<th>Type of treatment on PIM-1</th>
<th>(P(O_2)) (barrer)</th>
<th>(P(N_2)) (barrer)</th>
<th>(\alpha) (O_2/N_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cast from CHCl_3</td>
<td>580</td>
<td>180</td>
<td>3.2</td>
</tr>
<tr>
<td>cast from CHCl_3, immersed in MeOH for 5 days</td>
<td>1610</td>
<td>500</td>
<td>3.2</td>
</tr>
</tbody>
</table>
The selectivity of O$_2$ over N$_2$ is represented by $\alpha$, as given by: $\alpha = P(O_2)/P(N_2)$, where $P$ is the permeability of the gas.

It is believed that the alcohol causes swelling of the polymer matrix, possibly opening up cavities that were otherwise inaccessible to gas penetrants, and thus flushing out any trapped fugitive casting solvent. The matrix is supposed to maintain its structure for reasonably long after the methanol has been removed, even by vacuum drying. The mechanism of interaction between methanol and the PIM-1 polymer structure, and between alcohols and other guest molecules in general, is thus an area that needs exploring. Owing to the presence of electronegative N and O atoms, and also the $\pi$ electron system in the aromatic ring, PIM-1 is expected to behave spectroscopically both as an aromatic ether and as a nitrile, so that there is a high likelihood its interaction with protic and polar guest molecules is through hydrogen bonding with either or all of these sites. It is interesting to know if functional groups interact competitively or selectively with hydrogen bonding agents.

### 5.2 Evolution of the understanding of the hydrogen bond

In the later half of the 19th century, the concept of ‘attractive and molecular forces’ was used to try to explain deviations from ideal gas behaviour. In 1881, van der Waals law was used to explain real gas behaviour. Around 1887/8 studies on deviations from ideal liquid solutions led to the discovery that association effects are more likely to occur between certain functional groups, like alcohols for example. It was observed that these hydrogen-driven interactions exert significant influences on the physical properties of liquids. The anomalous behaviour of water, for instance, its melting and freezing points are 0 and 100 °C respectively as opposed to the expected (by extrapolation) -90 and -80 °C was ascribed to these interactions. In 1906, Oddo and Puxeddu发现了 the first intermolecular hydrogen bond as they tried to explain the properties of eugenol derivatives. In 1908, Weiner came up with an explanation of the bonding in ammonium salts. He suggested the structure: (H$_3$N---H)X, which essentially means the proton lies between NH$_3$ and X. The year 1913 saw Pfeiffer et al. try to find intermolecular links between OH and CO groups in 1-hydroxy-anthraquinone. Huggins and, separately, Latimer and Rodebush could have possibly come up with the theory of what is known as the hydrogen bond today. In 1920, Latimer and Rodebush were trying to rationalise the properties of highly associated liquids like water, hydrogen fluoride, the low basicity of ammonium...
hydroxide, and the dimerisation of acetic acid. In their explanation they used the Lewis dot formalism. It was not until 1931 however, when the descriptor ‘hydrogen bond’ was first used. Pauling used the term ‘hydrogen bond’ to interpret the structure of [F:H:F]. His chapter in ‘The Nature of the Hydrogen Bond’ in 1939 eventually brought the theory of the hydrogen bond into the mainstream.\(^{146, 147}\)

### 5.3 The Hydrogen Bond (HB)

The hydrogen bond (Figure 5.1) is an important factor in the conformational behaviour of molecules containing lone pairs of electrons which act as hydrogen bond acceptors, and polarised C-H bonds which act as hydrogen bond donors. For some time it was believed to be a purely electrostatic interaction, but research has shown there could be \(~5\%\) covalent character in O-H---O contacts, for example.\(^{145, 148}\) The hydrogen bond has contributions from electrostatic interactions between permanent multipoles, polarisation or induction interactions between permanent and induced multipoles, dispersion arising from instantaneous multipole-induced multipoles, charge transfer induced covalency, and charge correlation effects from short range repulsion due to overlap of the electron distribution. The contribution of each of these forces depends on the donor/acceptor system. This attractive interaction between two species is of the form shown in Figure 5.1:

![Figure 5.1](image.png)

**Figure 5.1** A diagrammatic representation of the hydrogen bond. D is the donor atom, H the hydrogen atom and A is the acceptor

Usually the donor, D and the acceptor, A are highly electronegative elements, for example O, N or halogens, and A possesses a lone pair of electrons.\(^{147}\) Other possible donors include CH and SH groups.\(^{143}\) Recent research has widened the scope of potential donors and acceptors to include H atoms in metal hydrides (forming dihydrogen bonding),\(^{149}\) C in CO,\(^{150}\) the bonding electrons of H\(_2\),\(^{151}\)
transition metals and noble gases.\textsuperscript{142} The HB is highly directional and bond strengths are typically in the range 10 – 30 kJ mol\textsuperscript{-1}, which is much higher than van der Waals forces (~1 kJ mol\textsuperscript{-1}), but lower than a chemical bond (50 – 1 000 kJ mol\textsuperscript{-1}).\textsuperscript{148} It is ubiquitous, and is known to give macromolecules like the DNA helix its stability and is responsible for the rigidity of molecular solids like sucrose.\textsuperscript{144, 146}

The D-H---A bond is characterised by stretching of the D-H bond in proportion to the hydrogen bond strength, transfer of a small amount of electron density from A to the molecule D-H, and the infra-red (IR) band corresponding to the D-H stretch shifts to a lower frequency (red shift), broadens and increases in intensity.\textsuperscript{147}

Structures of systems where the donor atom is carbon (C-H---A) have their conformational behaviour highly influenced by this hydrogen bonding. This hydrogen bond becomes stronger when the C-H bond is in the vicinity of electronegative atoms capable of partially withdrawing the electron cloud from the H atom, thus polarising the C-H bond further. The C-H---A hydrogen bond between chloroform and Lewis acids is archetypical.

Molecules like chloroform and alcohols readily form hydrogen bonds with ether groups\textsuperscript{152} or nitriles.\textsuperscript{153}

5.4 Characterisation of the hydrogen bond

Researchers have used a wide range of experimental and theoretical techniques to study the hydrogen bond.\textsuperscript{145, 147} The formation of a hydrogen bond in the D-H---A system weakens the D-H covalent bond, and this is the basis of many spectroscopic, structural and thermodynamic methods for the characterisation of the hydrogen bond.\textsuperscript{147} These methods include thermodynamic techniques, infrared spectroscopy, NMR spectroscopy, fluorescence spectroscopy and crystallography. Below is a brief description of some of these techniques.

5.4.1 Thermodynamic methods

Thermodynamic techniques were used during the early years of the discovery of the hydrogen bond. Studies on properties like anomalous boiling points, melting points, deviations from Raoult’s law, and abnormal $pK_a$ of acids, for example,
required basic application of thermodynamic techniques. With time, more advanced methods like direct calorimetry and van’t Hoff’s methods for the measurement of equilibrium constants were developed. These were however, only applicable to weak bonds of neutral D-H---A or zwitterions (D--H---A+). Stronger or negative charge assisted bonds were not accessible.

5.4.2 NMR spectroscopy

NMR is one of the most sensitive methods for detecting hydrogen bonding in solution. It is useful for characterising relatively strong bonds. Its high resolution means it can also be used to study weak donors like C-H or S-H, or aromatic acceptors. Technological advances in NMR, which include high magnetic field, multi probe, pulsed Fourier Transform, and the Nuclear Overhausser effect have greatly widened the scope of the technique. Solid state NMR gives this technique a further strength of being readily compared with X-ray crystallography.

5.4.3 Infrared (IR) spectroscopy

In the early 1930s, it was realised that D-H---A bond formation can be monitored using the IR red shift, $\Delta \nu$ induced by the hydrogen bond in the D-H stretching frequency, $\nu$ in relation to the standard value in the non-bonded state, $\nu^0$. According to Pimentel et al. the $\nu$(D-H) stretch offers the most sensitive, the most characteristic and one of the most informative manifestations of the hydrogen bond. Over time, IR has become the primary method for characterising the hydrogen bond in the liquid, solid or gaseous state. It yields information about the concentration of the hydrogen-bonded phase from peak intensities of the $\nu$(D-H) band, about geometrical arrangements of hydrogen bonded atoms, and hydrogen bond strengths. Use of Near infrared (NIR) and Far infrared (FIR) techniques has broadened the scope of application of the technique.

In infrared spectroscopy, the frequency of vibration of bonds depends on the masses of the atoms in the bond and the bond stiffness. This is expressed in Hooke’s law (Equation 5.1).

$$\nu = \frac{1}{2\pi} \left( \frac{k}{m_1 m_2 / (m_1 + m_2)} \right)^{1/2}$$
Where $v$ is frequency, $k$ is the force constant of the bond, $m_1m_2/(m_1 + m_2)$ is the reduced mass of the system, and $m_1$ and $m_2$ the masses of the two atoms.

Hydrogen bonding influences bond stiffness and consequently alters the vibration frequency. In alcohols, hydrogen bonding causes a shift in the O-H stretching and its harmonics from the usual 3700 – 3600 cm$^{-1}$ to 3500 – 2500 cm$^{-1}$. The interaction between the extra H atom and the rest of the molecule alters the reduced mass of the system and subsequently retards the OH vibration. It also causes an alteration in the intensity and half band width of the fundamental $\nu$(D-H) mode. The band shift can be correlated to a number of properties including bond lengths, enthalpy of formation of hydrogen bonds, or band intensity. It is not surprising, therefore that some researchers have resorted to using band shift as a measure of the base strength of donors. Thus infrared techniques can be used in detecting the sites of hydrogen bonding, and in quantifying it.

Attenuated Total Reflection Fourier Transform Infrared spectroscopy (ATR-FT-IR) enjoys a number of advantages over other techniques. It is an easy, rapid and relatively inexpensive spectral technique for qualitative analysis and for the quantitation of functionalities in organic materials. Compared to conventional Fourier Transform Infrared spectroscopy, it offers a superior signal-to-noise ratio and consequently high sensitivity. The sampling technique, ATR, enables the measurement of IR spectra of solids in their native state, eliminating the need for sample pretreatment as compared to KBr or mineral oil treatment sampling techniques. Ahmed et al. reported the use of Fourier-transform Infra-red (FT-IR) for the quantitation of natural antioxidants in vegetable oils. They used specialised software to perform a partial least squares (PLS) analysis and normalise the data to produce a calibration. Helmy et al. used ATR-FT-IR to identify and quantify polymorphs of Aprepitant, a substance P antagonist for chemotherapy induced emesis. By plotting the peak ratio of the second derivative of absorbance spectra against the weight percent of the polymorph in the standard, they constructed a calibration plot with polymorph standards. Their results compared well with X-ray powder diffraction (XRPD) data and actual values in standards. In inorganics, FT-IR has also been used to determine the concentration of cobalt in cobalt exchange zeolites.

Pandurangi et al. investigated the interaction of a number of hydrogen bonding agents by monitoring the vibrational modes in the bulk and surface of a silica substrate. They used the intensity of the silanol band and the shift in the broad
hydroxyl band as a quantitative measure of the interaction of surface groups. The interaction caused a shift in the broad silanol band near 3500 cm\(^{-1}\) and also a decrease in the sharp silanol band near 3747 cm\(^{-1}\). They found that the surface IR modes get perturbed more than the bulk IR modes in interaction with the hydrogen bonding agents.

Gray et al.\(^{165}\) used FT-IR to study hydrogen bonding in urea. They cited the existence of additional intermolecular interactions and spectral features as the problem that makes it difficult to study hydrogen bonding in large, complex bisurea organogelator molecules. As a result they resorted to studying simpler disubstituted monourea compounds. They found out that the amide band at \(~\)1620 cm\(^{-1}\) is not very sensitive to hydrogen bonding, it experiences less than 2 cm\(^{-1}\) shift. The C-N-H bend is quite sensitive to the strength of donated hydrogen bonds that restrict the motion of the hydrogen consequently lowering the frequency of the peak. Hydrogen bound ureas absorb at lower frequencies since the vibration of the urea hydrogen is retarded by participation in hydrogen bonding. The extent of retardation, and implicitly the magnitude of the frequency shift depend on the strength of the hydrogen bond.
5.5 Active sites for hydrogen bonding

Electronegativities are known to be one of the determinants of whether hydrogen bonding will occur or not, and also of the resultant bond strength.\textsuperscript{145} The Pauling electronegativities of H, N and O are 2.20, 3.04 and 3.14 respectively.\textsuperscript{148} Electronegativities that exceed 3.0 mean the atoms/groups are strong enough to display the full spectrum of hydrogen bond energies and geometries. Hydrogen bonds formed with the above acceptors are generally moderate in strength and characterised by 16.8 – 63 kJ mol\textsuperscript{-1} bond energies, H---A bond lengths of 2.2 – 1.5 Å, D-H-A bond angle of 130 – 180°, and a decrease in the infrared wavenumber $\Delta \nu$ (D-H) stretching of 10 – 20 %.

Wang et al.\textsuperscript{166} studied the interaction of OH and SH groups on 2-mercaptoethanol with methanol and dimethylsulfoxide (DMSO) using excess infrared spectroscopy. Because the proton-donating ability of the SH is less than that of the OH (as shown by their respective hydrogen bond acidities ($\alpha$): 0.00 for SH and 0.33 for OH),\textsuperscript{167-169} DMSO and methanol interact preferentially with the OH group.

In the current work, it is hoped that ATR-FT-IR will yield information about the identity of active sites on the PIM-1 polymer matrix, from which the possible structure of the intermediate species can be conjectured. Information about the relative strength of the hydrogen bond formed by interaction between an active site and a range of adsorbed molecules will also be obtained.\textsuperscript{170}

5.6 Hydrogen bonding in PIM-1

Apart from a study by Yampolskii et al.,\textsuperscript{131} there has been no systematic study of how the IR frequencies of the different functional groups in PIM-1 change upon hydrogen bonding in free solution or vapour at room temperature.

PIM-1 displays two vibrational bands that could potentially be used to monitor its hydrogen bonding state: the –O- stretch (1250 – 1350 cm\textsuperscript{-1}), and the –CN stretch (around 1265 cm\textsuperscript{-1}). Generally, the H---N and H---O bond lengths are 0.275 and 0.272 nm respectively.\textsuperscript{153} Yampolskii et al.\textsuperscript{131} carried out FT-IR and membrane permeation experiments to study the sensitivity of PIM-1 and polyetherimide (PEI) membrane properties to the presence of low molecular weight compounds that form hydrogen bonds. They showed that such hydrogen bonding causes conformational changes in the polymer matrix, which in turn has a bearing on the
performance properties of the membrane. Residual chloroform from the membrane casting stage, for example, was found to alter the positions and relative intensities of IR bands in the region of absorption of the $\text{C-O-C}'$ bonds. Removing the residual chloroform consequently changed the IR spectrum. They suggested this could be caused by conformational changes in the Ph-O-Ph' connector groups due to the heating and desorption of chloroform.\textsuperscript{131}

They also observed shifts in the 1250 – 1350 cm\(^{-1}\) band widths after impregnating the films with water and lower alcohols (methanol and ethanol), which they interpreted as conformational rearrangement in the polymer. Aromatic ethers are expected to show strong absorption in that region due to the C-O-C asymmetric stretching vibration.\textsuperscript{171} A shoulder around 3340 cm\(^{-1}\) is characteristic of the associates $\text{O-HO-R}$. The band due to the OH unperturbed by hydrogen bonding is expected in the region 3400 – 3600 cm\(^{-1}\), but they observed a marked difference between the OH band from ethanol (3670 cm\(^{-1}\)) and that from water (wide band at 3560 cm\(^{-1}\)). Interactions between polymer matrix and penetrant can be hydrogen bonding, weak dipole-dipole moments, or OH−π interactions.\textsuperscript{145} Hydrogen bonds between polymer chains and low molecular weight molecules can significantly affect the permeation and sorption parameters.\textsuperscript{68} Figure 5.2 shows the main IR peaks for the purpose of this study.

![Figure 5.2 The main IR peaks for untreated PIM-1. The nitrile group and the aromatic ether linkage will be the main focus of study.](image)

Figure 5.2 The main IR peaks for untreated PIM-1. The nitrile group and the aromatic ether linkage will be the main focus of study.
5.7 Experimental

PIM-1 (batch JDS057), synthesised as described in Chapter 2, was processed into films of thickness in the range 40 – 80 μm. Infra-red measurements were performed on ‘treated’ and ‘untreated’ PIM-1 membrane.

Untreated PIM-1 films

PIM-1 films were cast from chloroform as described in section 2.4.5.2. These were then soaked in methanol overnight before being dried in a vacuum oven at 120 °C for 4 h.

Treated PIM-1 films

The membrane treatment approach was three-pronged; (i) membrane treated with neat liquid alcohol, (ii) membrane treated with a mixture of alcohols or diluted alcohols, and (iii) membrane treated in alcohol vapour. A more detailed description follows.

5.7.1 Adsorption from the liquid phase

Adsorption of hydrogen bonding agents in the liquid phase was performed in two different ways. These are (a) adsorption from neat solution, and (b) adsorption from binary mixtures.

(a) Adsorption from neat solution

PIM-1 films (cast from chloroform by solvent evaporation as described in Chapter 2 and out-gassed at 120 °C for at least 4 hours before use) were soaked in about 10 cm³ of water, methanol, ethanol, propan-2-ol, butanol and phenol separately and left overnight in a tightly sealed container. The film was then air dried for up to 5 minutes just before making an IR measurement on the Bio-Rad FTS 6000 spectrometer. Shifts in aromatic ether peaks and peak intensities were recorded.

(b) Adsorption from binary mixtures

(i) A series of Methanol/Ethanol, Methanol/Water, Methanol/Propanol and Methanol/Butanol binary mixtures were prepared by adding successive 5 cm³
amounts of methanol to a total of 20 cm$^3$ of mixture. This was converted to mole fraction of methanol.

(ii) Similarly, a series of Water/Methanol, Water/Ethanol, and Water/Propanol binary mixtures were prepared by progressively adding 5 cm$^3$ of alcohol to a total of 20 cm$^3$. Amounts of alcohol were converted to mole fractions.

PIM-1 films were then soaked in each of these mixtures overnight in a sealed container. IR measurements were performed as above.

**5.7.2 Adsorption from vapour (chloroform and alcohols)**

For vapour adsorption the PIM-1 membrane was placed in a 1 cm internal diameter sample vial which was then placed in a 2 cm vial preloaded with about 10 cm$^3$ of the liquid (chloroform, water or alcohol) as shown in Figure 5.3. After a preliminary study, ATR-FT-IR measurements were made periodically every 12 hours.

![Figure 5.3 The experimental set-up for vapour adsorption onto a PIM-1 membrane](image)
5.7.3 ATR-FT-IR instrumentation

FT-IR spectra were recorded on a Bio-Rad FTS 6000 spectrometer equipped with an ATR setup, and annexed to a Whatman FTIR purge gas generator. The spectra were recorded in the attenuated total reflection (ATR) mode, with a resolution of 0.25 cm\(^{-1}\), a sensitivity of 1, and 5 scans in the range 4000 – 600 cm\(^{-1}\) were averaged for each spectrum. Before running the treated membranes, a PIM-1 membrane was run a few times to ascertain experimental repeatability and random error of the technique. Peak integration and spectra manipulation was performed using Win IP-Pro software before transferring the data onto MS Excel spreadsheets for further manipulation.
5.8 Results and Discussion

5.8.1 Repeatability of measurements

Before investigating the effects of the various penetrants on the PIM-1 matrix, ten repeat measurements were performed on untreated PIM-1 to establish the dispersion of the nitrile and the aromatic ether frequencies. The results are displayed in Table 5.2.

Table 5.2 Repeatability of measurements on untreated PIM-1 membrane

<table>
<thead>
<tr>
<th>Peak</th>
<th>Mean wavenumber, $\bar{x}$ (cm$^{-1}$)</th>
<th>CV $^\dagger$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrile (CN)</td>
<td>2239.46</td>
<td>0.02</td>
</tr>
<tr>
<td>Ether (O)</td>
<td>1265.35</td>
<td>0.03</td>
</tr>
</tbody>
</table>

$^\dagger$ The coefficient of variation, $CV = \frac{s}{\bar{x}} \times 100$ where $s$ is the standard deviation of the mean, $\bar{x}$ as described in section 3.2.1.1.

These mean values of the wavenumber were regarded as the baseline values for the purpose of determining any shifts. Shifts in wavenumber exceeding 0.38 cm$^{-1}$ for the aromatic ether group, and 0.40 cm$^{-1}$ for the nitrile group, suggest a real observable change in the conformational structure of the polymer matrix. This could possibly be the effect of hydrogen bonding between the penetrant and the pertinent functional groups on the PIM-1 structure. Another possibility is the existence of intramolecular interactions (e.g., nitrile-nitrile interactions) within the polymer structure.

The OH peak for water treated PIM-1 and for phenol treated PIM-1 has a rather high coefficient of variation. These were particularly noisy peaks even after smoothing and apodization. Another anomaly was observed in the ether peak wavenumber shift for these two hydrogen bonding agents and is discussed later.

5.8.2 IR spectral processing

Representative infrared spectra of treated and untreated PIM-1 films are shown in Figure 5.4 (a) and (b). The primary peaks of interest arising from the aromatic ether ($\sim$1264 cm$^{-1}$), the nitrile ($\sim$ 2240 cm$^{-1}$), are counterpoised against each other to show the frequency shifts. The peaks in the region 1000 – 1080 cm$^{-1}$ (not shown) could be due to intramolecular hydrogen bonding in the alcohols, and
intermolecular hydrogen bonding between the alcohols and water\textsuperscript{172}. The occurrence of significant spectral shifts between the membrane before and after treatment with solvent on the nitrile and ether peak regions provides evidence for structural change. The alcohol-treated membranes consistently exhibit an additional OH band at 3300 - 3500 cm\textsuperscript{-1} (not shown) that clearly distinguishes it from the untreated membrane, indicating that ATR can provide definitive identification of the two groups of membranes.

The interaction between alcohols and the nitrile and the aromatic ether groups is indicated not only by the change in intensities, but also by the changes in the frequency shifts, \( \Delta \nu \) as defined by the difference between the wavenumber after the shift and the baseline (Table 5.2). A positive difference indicates a shift to a higher wavenumber (blue shift) and a negative difference corresponds to a shift towards a lower wavenumber (red shift).
Sorption of Gases and Liquids by Polymers of Intrinsic Microporosity (PIMs)

Figure 5.4 Infra-red spectra for PIM-1 and hydrogen bonding agents, showing shifts in the (a) nitrile peak, and (b) ether peak
5.8.3 Neat liquid adsorption

Both the nitrile and aromatic ether functional groups in PIM-1 exhibit significant frequency shifts on interaction with alcohols, water, and chloroform (Figure 5.5). All the alcohols and water showed a red shift for the aromatic ether peak, and a blue shift for the nitrile peak. Chloroform and phenol showed red shifts for both functional groups. Considering the electronegativities ($O = 3.44$, $N = 3.04$)\(^{148}\) and hence the hydrogen bond lengths for the $N$---$H$ and $O$---$H$ HB, one would expect a stronger and consequently more dominant $O$---$H$ bond.

![Figure 5.5 Frequency shifts ($\Delta \nu$) of the (DH-X) band for different hydrogen bonding agents relative to the baseline values established in Table 5.2. The black bars represent the nitrile frequency shifts, and the red bars represent the aromatic ether frequency shift. Water and alcohols show a red shift for the aromatic ether group, and a blue shift for the nitrile group, chloroform and phenol show red shift for both the nitrile group and the aromatic ether group.](image)

Figure 5.5 shows an interesting pattern on the variation of the frequency shift with alcohol chain length. It appears that, as the alcohol chain length increases, so does the frequency shift up to ethanol, after which the frequency shift decreases. Perhaps this could be attributed to steric hindrance of the bulkier groups so that their access to the hydrogen bonding site is progressively restricted. Thereafter the frequency shift decreases with increasing chain length. The biggest difference in frequency shifts is between water and the alcohols...
except phenol. Further investigations on alcohol/water binary mixtures are reported in section 5.8.5.

Alcohols exhibit anomalous frequency shifts (blue shifts) on the nitrile group. There is a contestable hypothesis that this could be due to intramolecular nitrile-nitrile interactions rather than hydrogen bonding. There may be some nitrile-nitrile interactions in the unswollen state, so that the baseline value is red-shifted from the value that would be expected for a free nitrile. Swelling will move chains, and hence nitrile groups, further apart, leading to an apparent blue shift.

Blue shifts have been observed by Wojtkow et al. as they investigated the effect of temperature on butyl-alcohol mixtures. On performing IR spectroscopy on triformaldehyde (TFM), Lord et al. also observed a blue shift of the C-H stretch. These researchers however, did not explain this unusual phenomenon. An explanation of the blue shift was proposed by Hobza et al. who ascribed the descriptive nomenclature *improper blue shifting* hydrogen bond as opposed to the normal red shifting bond. They observed that the blue shifting hydrogen bond is accompanied by the shortening of the O-H bond. There are no fundamental differences between red and blue shifting hydrogen bonds. Joseph and Jemmims demonstrated that the D-H-A energy minimum can occur at a longer, equal or shorter D-H distance relative to the D-H fundamental. For the red shifting hydrogen bond, elongation of the O-H bond enhances the dipole-dipole attraction between the alcohol and proton acceptor, O or N. The electrostatic interaction is predominant and other terms like the charge transfer term are also significant. In contrast however, improper blue shifting hydrogen bonds the predominant stabilisation energy contribution is from the London forces term, which varies inversely with the sixth power of the separation between the centres of mass of the proton donor/acceptor system. To maximise this attraction, the O-H bond length shortens. Boldeskul et al. explain this occurrence in chloroform-nitro systems as an increase in the s character of the C-H bond owing to molecular deformation caused by intermolecular forces. Admittedly, this does not account for all systems involving improper blue shift hydrogen bonding, so additional terms are required to adequately explain this type of hydrogen bonding. In redefining the hydrogen bond, the IUPAC included the red shift as a criterion for hydrogen bonding with a caveat as a footnote.

Notwithstanding the foregoing possibility, that the nitrile group frequencies for alcohols are consistently blue shifted suggests a different kind of interaction
between the alcohols and these two functional groups. Perhaps this could be ascribed to the sterical orientation of these moieties on the PIM backbone. The structure of PIM-1 (Figure 5.6) is such that the nitrile nitrogen atoms are more exposed than the ether linkages. This might mean the nitrile groups are more likely to interact with each other in the swollen state of the polymer, and the adsorption of alcohols undermines this interaction.

![Image](image_url)

**Figure 5.6 The van der Waals model of PIM-1 showing that where the chain turns back on itself, the nitrile groups (blue spheres) come into close proximity.**

### 5.8.4 Relative strength of the hydrogen bond

Because the red shift is correlated to the hydrogen bond strength, relative magnitudes of frequency shifts have been used to compare hydrogen bond strengths. The larger the red shift, the stronger the hydrogen bonding causing it. This is because the vibration of a strongly hydrogen bonded atom will be more retarded than a weakly bonded one, resulting in a larger red shift. This being the case, the strength of the hydrogen bonds follows the order: water > phenol > chloroform > methanol > butanol > propanol > ethanol with respect to aromatic ether $\Delta \nu$.

Corollary to this, assuming the nitrile groups are also involved in hydrogen bonding, the larger the blue shift the stronger the hydrogen bonding. It follows then that the hydrogen bond strength is in the order: ethanol > methanol > butanol > propanol > phenol > chloroform > water, with respect to the nitrile $\Delta \nu$. 


If this assumption is refuted, these blue shifts might just be due to the reduction of nitrile-nitrile interactions by alcohol adsorption as alluded to earlier.

Pandurangi et al.\textsuperscript{158} used the difference in absorbance of the aromatic ether stretch, and the change in intensity, $\Delta \nu$ of the hydroxyl band in order to measure relative hydrogen bond strengths. They concluded that a plot of $1 - \sqrt{I_c / I_s}$ against $\Delta \nu$ gives the relative strengths of the hydrogen bonding due to the various agents,\textsuperscript{158} and they demonstrated that this is as good a comparator of bond strength as $\Delta \nu$.

**5.8.5 Adsorption from binary mixtures of alcohols**

To augment neat liquid adsorption and further investigate the hydrogen bonding between alcohols and PIM-1, a study of adsorption from binary mixtures of hydrogen bonding agents in the liquid phase was also undertaken as described in section 5.8.1. Binary mixtures of Methanol/Water, Methanol/Ethanol, Methanol/iso-Propanol and Methanol/n-butanol at increasing mole fraction of methanol, and Ethanol/Water, Propanol/Water, and Butanol/Water mixtures at increasing mole fraction of alcohol, were investigated.

**5.8.5.1 Methanol/Alcohol mixtures**

Figure 5.7 shows the plots of the mole fraction of methanol, $X_{\text{MeOH}}$ with ether frequency shift, $\Delta \nu(O)$ for the Methanol/Alcohol binary mixtures interacting with the aromatic ether group. As expected, all the binary systems show a red shift which increases with increasing methanol mole fraction. The presence of propanol appears to enhance the interaction of the OH group with the aromatic ether the most.
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Figure 5.7 The aromatic ether red shift as a function of mole fraction of methanol for Methanol/Water (blue diamonds), MeOH/Ethanol (brown squares), Methanol/isopropanol (green triangles), and Methanol/n-butanol (black dots) binary mixtures.

In Figure 5.8 however, the pattern is different. Except for the Methanol/Water system in which the blue shift initially decreases before reaching a constant value, the rest show a constant frequency shift around 1 cm⁻¹ with increasing mole fraction of methanol. This suggests a saturation at that point, which could possibly be the point at which the PIM-1 membrane has adsorbed enough methanol to reach its maximum swollen capacity.

Figure 5.8 The nitrile blue shift as a function of mole fraction of methanol for Methanol/Water (blue diamonds), MeOH/Ethanol (brown squares), Methanol/isopropanol (green triangles), and Methanol/n-butanol (black dots) binary mixtures.
It therefore would appear that the interactions (hydrogen bonding in the case of the aromatic ether group, and possibly nitrile-nitrile interactions in the case of the nitrile group) tendencies, and hence the relative strengths of the interactions between alcohols and the two sites is contingent upon the environment in which the PIM-1 membrane is. PIM-1 membranes are known to be selective towards organic penetrants.\textsuperscript{30, 33, 48}

5.8.5.2 Water/Alcohol mixtures

Figure 5.9 (a) – (c) shows the variation of aromatic ether and nitrile frequency shifts for methanol/water, ethanol/water and propanol/water binary systems. Because butanol is not miscible with water, this binary system was omitted. Invariably, for each system, the ether frequency is red shifted. This red shift decreases to a constant with increasing mole fraction of alcohol. This is consistent with the red frequency shifts for alcohol treated PIM-1 reported in section 5.8.3.

For the nitrile group, the frequency shift increases and reaches a maximum, after which it decreases. In the case of the methanol/water and ethanol/water systems this maximum is close to an alcohol mole fraction of 0.2, whereas for the propanol/water system it is shifted towards a mole fraction of 0.5.
Sorption of Gases and Liquids by Polymers of Intrinsic Microporosity (PIMs)

Figure 5.9 The variation of the aromatic ether (blue diamonds) and nitrile (brown squares) frequency shifts with mole fraction of alcohol for (a) Methanol/Water, (b) Ethanol/Water, and (c) Propanol/Water binary mixtures.

Water and alcohol are a miscellany of hydrogen bonding, which determines the physical properties of these liquids. Mole fraction additivity of the dipole moment...
is not observed for the alcohol/water systems. Alcohols are associated liquids and the degree of association and the form of the associates change on going from lower to higher alcohols.\textsuperscript{172} There are linear and cyclic associates, and the relative quantities formed in methanol are less than those in the ethanol and so on. It must be assumed that when small quantities of methanol are added to a higher alcohol, the packing of the higher alcohol becomes closer, as a consequence of the interaction of the linear associates of the alcohols and the formation of complex cyclic associates. This results in the average dipole moment being lower than the average dipole moment of the component alcohols.\textsuperscript{177}

5.8.6 Adsorption from vapour

Parallel to adsorption from solution, alcohol and chloroform adsorption was also investigated in the vapour phase as described under section 5.7.2. The results are presented below.

5.8.6.1 Water vapour and alcohol vapours

Like in the liquid phase, alcohols in the vapour phase appear to cause as much frequency shift for both the nitrile group and the aromatic ether group as in the liquid phase. Save for methanol vapour, ether frequency shifts generally oscillate around -1 cm\textsuperscript{-1} (Figure 5.10 (a)). Figure 5.10 (b) shows that, except for methanol, the frequency shifts for the nitrile peak monotonically increase towards 1 cm\textsuperscript{-1}. For methanol vapour it decreases towards this value before rising again. This might suggest that as the PIM-1 membrane adsorbs increasing amounts of alcohol, it swells up pushing the nitriles further apart until they cannot get any further.

Methanol, being the smallest of the alcohol homologous series seems to penetrate the PIM-1 structure and interact more. Perhaps this is why it is more suitable for use in flushing out residual solvent from PIM-1 powder (fugitive solvent left over from synthesis) and films (solvent left over from film casting).
Figure 5.10 The variation of the (a) aromatic ether, and (b) nitrile frequency shifts with the time of exposure to alcohol vapour. MeOH (blue triangles), EtOH (brown squares), PrOH (green triangles), and BuOH (black dots)

5.8.6.2 Chloroform vapour

Figure 5.11 (a) and (b) shows the IR peaks for nitrile and aromatic ether groups respectively for a PIM-1 membrane treated with chloroform vapour. There is shift in frequency that is monitored with time of exposure of the membrane in Figure 5.12.
Figure 5.11 Comparison of chloroform treated and untreated PIM-1 membrane, showing the red shifts in the (a) nitrile, and (b) ether peaks. The purple peaks are the untreated PIM-1 and the blue ones are the chloroform vapour treated PIM-1.
As shown by the larger red shift for the aromatic ether group than the nitrile group (Figure 5.12), chloroform vapour preferentially interacts with the aromatic ether group compared to the nitrile group. This could further support the hypothesis that nitrile groups might just be involved in intramolecular nitrile-nitrile interactions rather than in hydrogen bonding. Studies performed by Yampolskii et al. on PEI membranes and chloroform vapour showed that hydrogen bonding on the ether group is thermodynamically more favourable than on the N atom. There are obvious structural differences between PEIs and PIM-1, chief among which is the presence of a nitrile group in PIM-1 whereas PEI has a nitrogen linkage. Nevertheless, this phenomenon is repeated here with PIM-1.

Figure 5.12 Variation of nitrile (red triangles) and aromatic ether (black diamonds) frequency shifts with time of exposure of PIM-1 membrane to chloroform vapour.
Hydrogen bonding in PIM-1 can be summarised by Figure 5.13, which shows alcohol or water \((R = H)\) molecules interacting with the nitrile and ether sites.

![Figure 5.13](image)

**Figure 5.13** The active sites for hydrogen bonding in PIM-1. The N groups are more likely to form nitrile-nitrile interactions in the unswollen state of the polymer.
5.9 Conclusion

In this chapter, ATR-FT-IR spectra of PIM-1 membranes exposed to different liquid mixtures and vapours of alcohols and chloroform were analysed to better understand how the hydrogen bonding changes the nitrile and ether stretches of this polymer. The technique has been used successfully to characterise hydrogen bonding in PIM-1.

Adsorbate-adsorbent interactions in PIM-1 polymer/liquid or polymer/vapour systems are readily characterised by ATR-FT-IR because the sensitivity of the ether band stretching, $\nu(O)$, to changes in hydrogen bonding makes this an effective indicator. The IR frequencies of this functional groups shifts when engaged in hydrogen bonding, the extent of which depends on the degree of hydrogen bonding to the group.

The two possible hydrogen bonding sites in PIM-1 (the nitrile group and the aromatic ether group) have different interaction mechanisms in the presence of hydrogen bonding agents. The results show that alcohols cause a blue frequency shift on the nitrile group and red shifts on the aromatic ether group, while chloroform vapour causes a red shift for both functional groups.
Chapter 6: Conclusions and Recommendations
Chapter 6: Conclusions and Recommendations

6.1 Introduction

This chapter presents an overall conclusion and gives recommendations arising from the research.

6.2 Conclusions

Synthesis of PIM-1, PIM-2, PIM-7 and Thioamide PIM-1 was a success as proved by the characterisation. These materials were also proved to be microporous.

A gas adsorption characterisation methodology for microporosity was developed and validated.

A variety of pore size distribution models were compared. It was concluded that the Horvath-Kawazoe (HK) method was the most applicable since it matched closely with XRD data obtained for 3,3’,4,4’-tra(trimethylsilylethynyl)biphenyl. The Dubinin-Astakhov, the DFT and the BJH models over-estimate the pore widths. Their use in characterising micropores does not yield functional data. In the Horvath-Kawazoe with slit pores, use of the Ross-Olivier parameter (which uses a lower value of the magnetic susceptibility for carbon, 1.05 x 10^{-29} instead of 1.35 x 10^{-28} used for the original HK model), and effectively lowers the interaction parameter) underestimates the pore widths. Using the Ross-Olivier parameter with cylindrical geometry (Saito-Foley) however, gave results comparable to the HK model with slit pore geometry.

The traditional N\textsubscript{2} gas sorption at 77 K was complemented with CO\textsubscript{2} adsorption at 273 and 303 K to yield more pore size distribution data. This novel approach proved useful for characterising the microporosity of the materials under study, and could be applied to related materials.

Film formation in PIM-1 was found to effectively reduce the N\textsubscript{2} uptake characteristics of the polymer. Films showed decreased kinetics compared to powders. Residual casting solvent, coupled with the high density of the surface layer of the film, could possibly be the cause.

The structure of a polymer material was found to influence its gas sorption behaviour. PIM-2, which structurally differs from PIM-1 owing to the presence of an sp\textsuperscript{3} carbon joining the biphenyls, has less microporosity than PIM-1. This is
because the sp³ carbon allows rotation of the rings and facilitates more efficient packing. Triptycene based PIMs are network polymers with a rigid, fused ring skeleton and three-fold symmetry. This enhances their microporosity, which is greater than that of PIM-1 as shown by the high BET surface areas.

A slight but significant increase in the pore widths was observed upon introducing the ethano-anthracene unit into PIM-1 to make the copolymer series PIM1-CO1. The ethano-anthracene unit provides significant structural differences from PIM-1 resulting in less dense packaging of the polymer chains that should result in a higher free volume.

The microporous character of a PIM-1 sample and a PIM1-CO1-40 sample as studied by N₂ sorption, Xe sorption, ¹²⁹Xe NMR, and PALS, was found to depend not only on the purification process, but also on the analysis history. A reduction in the microporosity of PIM-1 in the region 0.6 – 0.7 nm pore width was observed, and this was removed upon conditioning and relaxing the polymer through methanol treatment and a heating cycle.

ATR-FT-IR was successfully used to study the interaction between hydrogen bonding agents (water, chloroform, and smaller chain alcohols) and the aromatic ether linkage and the nitrile group on a PIM-1 membrane. This investigation found evidence of hydrogen bonding between the H of these agents and the aromatic ether and the nitrile groups on PIM-1. Alcohols form blue shifting hydrogen bonds with the nitrile group in PIM-1, which is an unusual phenomenon. This could be due to a red shifted base line caused by intramolecular nitrile-nitrile interactions. Chloroform and phenol exhibit red shifts with both the aromatic ether linkage and the nitrile group. Water gives a red shift with the ether linkage, and a blue shift with the nitrile group.

Considering these achievements, it seems reasonable to conclude that the research objectives, as outlined in Chapter 1, have been successfully achieved.
6.3 Recommendations

Gas sorption measurements on PIMs using the ASAP 2020, the Coulter 3100 and the Coulter 3200 should use an outgas time of 8 hours and a temperature of 70 °C after drying the sample in a vacuum oven at 120 °C for at least 4 hours. This temperature/time regime should be tailored for each material other than PIMs depending on its thermal properties.

A combination of PSD data for N₂ at 77 K and CO₂ at 303 K (and high pressure) can be routinely used to characterise microporosity because it gives a more complete picture of the distribution of pore widths.

The H-K model assumes the microporous material to comprise of parallel graphite slabs of infinite length and width. This gives satisfactory data especially for comparison purposes. However, in order to get more accurate PSD data, determination of the exact physical parameters characteristic of the material under study should be carried out. These physical parameters include polarisability and magnetic susceptibility.
Sorption of Gases and Liquids by Polymers of Intrinsic Microporosity (PIMs)

References

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