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# **Review on Polymers of Intrinsic Microporosity: Their Classification, Synthesis, Properties, and Applications**

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Abstract: Polymers of Intrinsic Microporosity (PIMs) constitute another class of amorphous microporous polymers. PIMs display high SSA (specific surface area) (due to their rigid and contorted molecular structure (Fig. 1a), which prevents efficient packing. In particular, PIMs do not possess rotational freedom along the polymer backbone, which ensures that the macromolecular components cannot rearrange their conformation. Several proposed methods for synthesizing different polymers have been recorded due to their potential properties and wide applications in recent years. This review will cover the origin of the early work on PIMs, their synthesis and structural characterization, properties, and potential applications that are broadly recognized as a potential next generation membrane material for gas separations due to their ultra-permeable characteristics. This mini review aims to provide an overview of these materials, from science of its chemistry to applications. PIMs-based gas separation membranes applications of this type cover a wide spectrum including their gas diffusion mechanisms and separation performance, and many other fields such as using PIM membrane in water purification from chemical pollutants. Membrane separation process is cost-effective and environmentally friendly with small physical footprints. Interests of membrane technology have been growing increasingly in past two decades. Key areas that membranes are at play include carbon dioxide (CO<sub>2</sub>) capture, nitrogen generation, hydrogen/helium recovery, natural gas sequestration and biogas purification (Bernardo, Drioli, & Golemme).



Figure-1a Molecular structure of PIM-1

**Keywords:** Polymers of Intrinsic Microporosity (PIM), SSA (specific surface area), Synthesis, Applications, Water Treatment, membrane, biogas, natural gas, environmentally friendly, pollutants, purification, CO2 capture, permeable membrane

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#### 1. Introduction

Intrinsic microporosity in polymers is defined as "a continuous network of interconnected intermolecular voids, which forms as a direct consequence of the shape and rigidity of the component macromolecules" (O. M. Ilinitch, V. B. Fenelon, A. A. Lapkin, L. G., Okkel, V. V. Terskikh, and K. I. Zamarra, 1999), (N. B. McKeown and P. M. Budd ". i., 2009). Nowadays, one of the most common problems faced by humans over the world is water contamination. Geological and anthropogenic/human-made are mainly classified and considered primary water pollution sources (Fawell and Nieuwenhuijsen, 2003). According to numerous studies in the literature, freshwater resources have been recently contaminated with various contaminants due to human activities by advancing industrial growth and technology (Kumar and Puri, 2012). In the last three decades, several approaches have been efficaciously suggested to treat pollutants/toxic chemicals from the water system to avoid environmental impact (Elwakeel et al., 2020). Among the possible techniques, using adsorbents via the adsorption method has been superior to other methods (Alnajrani and Alsager, 2020, Budd et al., 2005, Satilmis, 2020). The used adsorbents can also be categorized into different synthetic or natural materials (Doble, 2007, Mohan and Pittman Jr, 2007). In recent years, 'Polymers of Intrinsic Microporosity, PIMs' such as synthetic adsorbents have been efficiently applied to remove various chemical pollutants in the environment (Ye et al., 2020). Several proposed methods for synthesizing different PIMs materials have been recorded due to their potential properties and wide applications in recent years. This review offers detailed background information on the PIMs materials and their synthesis approaches. The rapid recent progress in the synthesis of microporous network polymers has been reviewed extensively (R. Dawson, 2012), (R. Dawson, 2012). In contrast, this present paper will focus on polymers that do not require a network of covalent bonds in order to demonstrate microporosity-the so-called polymers of intrinsic microporosity (PIM).

#### History of Polymers of Intrinsic Microporosity (PIMs)

An invention of a new polymer such as polybenzodioxins combining spiro-centers with a high smooth permeability was initially synthesized by Sing (1985). Microporosity denotes materials that included many pores of dimensions (< 2nm) (Sing, 1985). The idea for PIMs developed from the work on phthalocyanine materials carried out at The University of Manchester during the 1990s. Phthalocyanines are large aromatic macrocycles related to the naturally occurring porphyrins, and metal-containing phthalocyanines can demonstrate useful catalytic activity, especially for oxidation reactions (N. B. McKeown. C., 1998). However, in the solid state, the catalytic performance of phthalocyanines is hindered by the face-to-face aggregation of the macrocycles. In 1998 we designed a network polymer consisting of phthalocyanines fused together with spirocyclic groups that would produce a highly porous material in which each adjacent macrocycle would be orthogonal to its neighbor (N. B. McKeown H. L., 2001). "Polymers of Intrinsic Microporosity," which is introduced and abbreviated as "PIMs," is a new category of a membrane-forming polymer and relatively a novel type of macromolecule. PIMs involved a high free volume, which is not efficiently filled like linear polymers and causes to increasing their intrinsic microporosity. PIMs are introduced as materials having contorted shapes and inherent rigidity property. Thus, these properties cause to not filling space absolutely like typical linear polymers. These properties lead to enhancing and rising intrinsic microporosity property (Budd et al., 2004a, Budd et al., 2004b). They were firstly named PIM-1 (Budd et al., 2004b), mentioned and synthesized in chemistry by Budd et al. (2004a). Consequently, these properties provide a direct new formulation of the component with macromolecule's shape and rigidity (Ilinitch et al., 1999, Shaver, 2014).

#### **Designing and Synthesis of PIMs**

PIMs classified and known as a porous organic polymer (POP), have microporous materials properties. PIMs are rigid and contorted macromolecular chains owing to incompetent packing voids (McKeown, 2017). PIMs are easily dissolved in organic solvents as they are not involved in a network of cross-linked bonds. In general, several chemical polymerization reactions could be applied to produce different PIMs. Simultaneously, few of them are practically confirmed to be efficacy for producing solution-processable components, including cast films. Thus, the recorded result from previously documented data showed that PIMs had been sufficiently synthesized by utilizing three categories of polymerization reactions (McKeown, 2017). Among them involves the polymerization formation through imide linkages, Tröger's base, and dibenzodioxin between monomeric units (Carta et al., 2014b, McKeown, 2017).

## 1.1. Polymerization Utilizing Dibenzo dioxane Formation

The first PIM was proposed, synthesized by Budd et al. (2004b), and named the archetypal PIM, PIM-1, resulting from a new nucleophilic aromatic substitution (SNAr) mechanism. In this method, tetrafluoroterephthalonitrile (TFTPN) and 5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-pimobendane (SBI) which were two obtainable and known monomers were used to achieve the first PIM-1 (Budd et al., 2004b). Figure 1 shows detailed information on the nucleophilic substitution reaction between TFTPN and SBI (McKeown, 2017).



Figure 1: illustrates the first production of PIM-1 resulting from a nucleophilic substitution reaction between TFTPN (B1) and SBI (A1) (Budd et al., 2004b).

The formed product via this polymerization reaction provided a fused-ring linkage group with adequate capability to offer solution-processable ladder polymers. The synthesized polymer had a high average molecular mass (Budd et al., 2004a, Budd et al., 2004b). A halide-containing monomer (e.g., F, CN) is needed to occur aromatic nucleophilic substitutions and activate the stepwise of an electron-withdrawing (Eastmond et al., 2001).

The firstly proposed method is also introduced as the production via the low-temperature process. The TFTPN and SBI monomers with the same quantity (3 mmol as optimal) were mixed in the used solution of dimethylformamide (anhydrous DMF). Simultaneously, dry chemical such as dryK2CO3 was directly used as an excess amount and applied as a fine powder at about 60 °C for 1-3days. The uses of low temperature keep the DMF and prevent its degradation to dimethylamine. Applying a high concentration of monomers has a vital role in forming insoluble cross-linked polymers. Different PIM-1 materials could be obtained due to applying alternative precursors monomer such as tetra-silyl ether via a fluoride-mediated reaction (Kricheldorf et al., 2005, Zhanget al., 2015). Different studies have been documented to synthesize various PIM materials via this polymerization process, applying dibenzodioxins formation. The final PIMs materials produced via this method were readily soluble in varying organic solvents ordered as follows CHCl<sub>3</sub>, THF, quinoline, m-cresol, and DMF (McKeown, 2017). The measured surface area based on the BET method was also in the range of 203-889 m<sup>2</sup>/g (McKeown, 2017).

#### 1.2. Polymerization Utilizing Tröger's base formation

A new and applicable polymerization approach established on Tröger's base (TB) production could be

applied to obtain different PIMs materials with a high average molecular mass (Carta et al., 2014b). The new polymer production starting from the TB formation method can be obtained using aromatic diamine with dimethoxymethane monomer (Figure 2). This reaction is simple and occurs owing to applied trifluoroacetic acid, leaving under appropriate conditions (at 0 °C) (Du et al., 2008). This polymerization method is known and formally called 2,8-dimethyl6H,12H-5,11- methanodibenzo [b, f] [1,5] diazocine. The varying property of the formed PIMs was designed and based on the different monomers used. The TB formation step is a premium due to forming the TB linkage group (fused-ring) for the final PIM product. Appling the TB formation is a successful polymerization reaction suitable for polymer production with high rigidity and prohibition conformational freedom. Figure 2 illustrates the novel PIMs synthesized utilizing Tröger's base polymerization (Carta et al., 2014b, McKeown, 2017).



Figure 2: illustrates the novel PIMs synthesized utilizing Tröger's base polymerization (Carta et al., 2014b, McKeown, 2017).

Various material products associated with this type of polymerization were documented from previous studies (Carta et al., 2014a, Carta et al., 2014b). Obtained results verified that polymers were readily soluble in CHCl3 solvent. The measured surface area based on the BET method was also in the range of 270-1028 m<sup>2</sup>/g (McKeown, 2017).

#### 1.3. Polymerization Utilizing imide formation (PIM-polyimides)

Polyimides (PIs) are mainly classified as an essential polymer category for a wide range of applications. These polymers are obtained and synthesized through the well-organized production of imide linkages between typical monomers (Figure 3) such as diamine (D) and dianhydride (E). PIs formation can also be utilized to achieve various PIMs materials (McKeown, 2017). The produced polymer is produced base on PIs formation, introduced, and classified PIM-PIs materials. To form a rigid PIM-PIs material, at least one of the used monomers has to be a site of contortion. Furthermore, diamine monomers included two large substituents neighboring amine groups are essential to limit rotation about the carbon-nitrogen (C-N) bond of the formed imide linkage. Thus, polymers (PIM-PIs materials) with a high level of intrinsic microporosity can be efficiently obtained via the proposed monomers (Ghanem et al., 2009, Ghanem et al., 2008). Figure3. illustrates the novel PIMs synthesized utilizing PIs formation (diamine E6, and dianhydride, D8 monomers) (McKeown, 2017).



Figure 3: illustrates the novel PIMs synthesized utilizing PIs formation (McKeown, 2017, Rogan et al., 2014).

Many polymer materials related to PIM-PIs were synthesized and mentioned from previous studies (Ghanem et al., 2009, Ma et al., 2013, Swaidan et al., 2014). Recorded results from previous studies verified that polymers were readily soluble in the CHCl3 and THF organic solvents (Ghanem et al., 2009, Ma et al., 2013, Swaidan et al., 2014). The measured surface area based on the BET methodwas in the range of 190-840 m<sup>2</sup>/g (McKeown, 2017). In another research, Ghanem et al. (2009) proposed a novel procedure to synthesize a range of PIM-PIs materials. Different aromatic diamines of a bis(carboxylic anhydride) were successfully applied in the proposed reaction. The obtained results of PIM-PIs provided high surface area and thermal stability (Ghanem et al., 2009).

#### 1.4. Post synthetic modification of PIMs

Many new PIMs materials can be obtained through the modification of another PIMs product. Postsynthesis reactions were introduced as an exciting approach and mainly applied to the originally PIM-1 to form new polymers with intrinsic microporosity. Structure modification of the original PIM-1 compound based on improving chemistry on the attached nitrile group (Figure 4) could be carried out to produce various polymers. The post chemical reaction via in situ hydrolyses of the attached CN groups of the applied PIM-1 was documented to form a new polymer (Figure 4, i-viii) or carbonylated PIMs materials (Du et al., 2009). Under basic conditions, various products of PIMs materials (Figure 5) with differential properties could be easily achieved via post-syntheticmodification of PIM-1 (McKeown, 2017).



Figure 4: illustrates different PIMs synthesized utilizing a post-synthetic modification of PIM-1(Du et al., 2009, McKeown, 2017).



Figure 5. Representative structures of recently reported PIM–PIs in the literature, (Yingge Wang, 2021)

## 2. Characterization of PIMs

#### 2.1. PIMs Structural Characterization

Different analytical techniques such as gel permeation chromatography (GPC), Fourier-transform infrared spectroscopy (FTIR), and nuclear magnetic resonance (<sup>1</sup>H and <sup>13</sup>C NMR) have been successfully carried out to characterize the chemical structure of PIMs components (McKeown, 2012). GPC is applied to calculate and estimate the approximate number average (Mn) and weightaverage (Wn) molecular mass of the examined PIMs. However, FTIR, <sup>1</sup>H, and <sup>13</sup>C NMR are utilized to detect H and C elements in the polymer structure, polymerization degrees (DPs) in polymers, and identify the polymer proposed structure (Lee et al., 2016, Makhseed et al., 2012). Matrix-assisted laser desorption ionization mass spectrometry can be useful for determining the presence of cyclic oligomers and the nature of the end-groups.

## 2.2. Characterization of PIMs Porosity

Detailed information on microporous structure characterization of PIMs can be investigated through different practical and theoretical analyzing methods. Among them includes gas sorption analysis, positron annihilation lifetime spectroscopy (PALS), and computer simulation (McKeown, 2012). The nitrogen gas adsorption/desorption process is well introduced as the Brunauer– Emmett–Teller (BET) method and performed at liquid N2 temperature (77 K) to characterize the produced microporous materials. Efficient adsorption of nitrogen gas (N2) by the examined materials at low levels of relative (P/P<sup>o</sup>) is clear evidence to indicate that the analyzed material is a microporous PIM (McKeown, 2012). Figure-6 illustrates the process of adsorption/desorption of N2 gas by PIMs materials.



Figure 6: illustrates the process of measuring the N2 adsorbed (black filled cycles) and desorbed (white empty cycles) on examined PIMs materials at 77 K (McKeown, 2012).

A graphical illustration for the solid-state of the examined PIMs macromolecules can be given utilizing computer simulations (Heuchel et al., 2008). A metastable particle introduced as *Ortho*- positronium (*o*-Ps) can be obtained by the direct reaction between an electron with a positron. The *o*-Ps can also be applied to investigate free and accessible volume in solid materials. The average lifetime of o-Ps in a vacuum is equal to 142 ns, while its lifetime is decreased within sold mater. Annihilating of *o*-Ps via encounter electrons is happen and causes reducing the *o*-Ps lifetime. *o*-Pso-Ps can fill free volume holes available in the examined polymers. Results verified that the decrease in the *o*-Ps lifetime is proportional to decreasing accessible real hole size in the analyzedporous polymers (Tao, 1972). More than one *Ortho*-positronium is required and used to measure free volumes of PIM-1 polymers due to high free volume availability (Staiger et al., 2008).

## **3. PIMs Properties**

#### 3.1. Solubility

PIMs were generally distinguished and introduced as readily soluble materials in many popular solvents at room temperature. It means that they do not necessitate adding solubilizing groups to enhance solubility like other polymers (McKeown, 2012). However, for PIMs it appears that the rigid and contorted macromolecular structures help to reduce intermolecular cohesive interactions by limiting the number of close contacts between polymer chains. The relative flexibility of the spirobisindane unit may also assist in solubility. The rigidity and contorted structure aremainly responsible for the degree of IPMs solubility. It may also be attributed to the fact that the polymer chain is contorted only within two dimensions allowing the polar nitrile groups to interact more fully thus increasing polymer cohesion, whereas soluble PIMs form random coils in all three dimensions. Chloroform and tetrahydrofuran are commonly low-boiling solvents that speedily dissolve most PIMs materials (Yin et al., 2019).

#### 3.2. Thermal Properties

Thermal analytical techniques such as differential thermal calorimetry (DSC) and thermal dynamic mechanical analysis (DMTA) can be used to investigate the thermal analysis and stability of synthesized PIMs materials that shows no glass transition temperature or other thermal transition below its decomposition at around 450°C (P. M. Budd E. S., 2004).

A tensile storage modulus of ~1 GPa, a tensile strength of 45–47 MPa, and a strain of 10%-11% at breakage have been reported for PIM-1. The results applying DSC and DMTA verifies no glass transition temperature during the analysis of PIM-1. They also show no thermal transition lower than its decomposition temperature (~ 450°C) (Budd et al., 2004a).

#### 3.3. PIMs Microporosity

PIMs microporosity and their specific solid surface area are measured due to utilizing the BET technique. Based on analyzing samples with different techniques, obtained results via the BET method verified that that investigated PIM-1 materials included high specific/active surface arearanging from 720 to 875 m<sup>2</sup> g<sup>-1</sup> (Bezzu et al., 2012, Makhseed et al., 2012). The recorded results associated with the surface area from previous studies confirmed that the surface is of PIM-1 ismatches few PIMs materials or higher than most of the PIM's material in terms of availability of surface area (Bezzu et al., 2012, Makhseed et al., 2012).

## 4. Applications of PIMs

As PIMs has a uniquely combine properties of being a microporous material, and they can selectively take up and transport molecular species, with the solution processability of a polymer. That made it center of interest for a number of applications.

## 4.1. Membranes

Over the past 2 decades, PIMs have been documented, investigated, and widely applied in many scientific fields due to the availability of significant properties (Ye et al., 2020). PIMs are distinguished with various properties owing to the availability of high free volume, active surfacearea, microporosity, microcavity, easy fabricability, and grater hydrophobicity (Zhang et al., 2018). The summarized applications associated with PIMs are shown in Figure 7 (Ye et al., 2020). These potential unique properties related to PIMs materials provide prospective applications in many fields. Among them includes pervaporation (PV), gas separation (GS), and nanofiltration (NF) (Ye et al., 2020, Zhang et al., 2018). PIMs are known as innovative types of microporous materials that have been effectively applied in gas separation areas from different industrials (Zhang et al., 2018).



Figure 7: The summarized applications associated with PIMs materials (Ye et al., 2020).

PIMs were efficiently employed as selective gas separation membranes in many industrial processes (Budd et al., 2005, Lee et al., 2016). GS in membrane separation is the most commonlyutilized area of PIMs (see Figure 7). According to examined studies, PIMs materials could be widely applied to transport ion /molecule through their available channels and permit gaseous/solids through their pores (Marken et al., 2020). In the Web of Science database, many published papers related to PIMs on membrane and gas "GAS" were previously documented (Ye et al., 2020) during the last decade (Figure 8).



Figure 8: illustrates the published articles percent recorded in the Web of Science database associated with membrane applications of PIMs (PIMs membrane application related to nongas, NOT GAS and gas, GAS) (Ye et al., 2020).

## 4.1.1. Pervaporation (PV) Membranes

In pervaporation, the feed is a liquid mixture and the permeate is removed as a vapour, which canthen be condensed into a liquid or solid at lower temperature. The driving force for transport comesfrom application of a vacuum or sweep gas to the permeate side of the membrane. An advantage of pervaporation is that it can be used to break an azeotrope. Commercial pervaporation plants, for example, for dehydration of ethanol/water mixtures, commonly employ hydrophilic membranes. However, there is increasing interest in hydrophobic membranes for waste-water treatment and for the separation of organic-organic mixtures. Pervaporation was the first application of PIM membranes to be investigated. PIM-1 was shown to form a hydrophobic membrane, selectively transporting organics, such as phenol and aliphatic alcohols (i.e., ethanol and butanol), from mixtures with water [ (Yingge Wang, 2021). High flux, coupled with good separation factor and stability, makes this a promising area for further development.

#### 4.1.2. Organic Solvent Nanofiltration (OSN) Membranes

Nanofiltration is now a well-established technology for treating aqueous solutions by retaining molecules above a certain size. Unlike pervaporation, there is no phase change on permeation. An area of particular interest for new polymers such as PIMs is that of solvent-resistant nanofiltrationfor the treatment of organic mixtures, where the aim is to operate a continuous reaction whilst extracting products but retaining a large molecular catalyst (S. V. Adymkanov Y. P., 2008). Membranes of PIM-1 and PIM copolymers show real promise in this respect (] M. Priske, 2012), (D. Fritsch P. M., 2012). Cross-linking methodologies (see below) may play an important role to enhance the stability of PIM OSN membranes especially for those organic solvents for which the PIM demonstrates solubility.

#### 4.1.3. Gas Separation (GS) Membranes

Polymer membranes offer an energy-efficient method for many gas separations as they do not require thermal regeneration, a phase change, or active moving parts in their operation (Y. P. Yampol'skii, 2006). In membrane gas separation, the driving force comes from a pressuredifference across the membrane (Baker, 2002). Commercially important membrane-based gas separations include O<sub>2</sub> and N<sub>2</sub> enrichment of air, hydrogen recovery from ammonia production (predominately H<sub>2</sub> from N<sub>2</sub>) or hydrocarbon processing (e.g., H<sub>2</sub> from CH<sub>4</sub>), and the purification of natural gas (predominantly CO<sub>2</sub> from CH<sub>4</sub>). However, polymers suffer from a well-defined trade-off between the desirable properties of permeability and selectivity for the required gas component. Presently, commercial gas separation membranes are based on a few well-established

polymers with low permeability and high selectivity; therefore, large membrane areas are required to compensate for lack of permeance. This means that existing polymer membranes are not currently competitive with other technologies for large-scale gas separations. For any given gas pair, the trade-off between permeability (i.e., permeance multiplied by membrane thickness) and selectivity (S. V. Adymkanov Y. P., 2008), (expressed as a ratio of permeabilities) may be represented by a double-logarithmic plot of selectivity against the permeability of the fastest species (Figure 9). In 1991, Robeson delineated an empirical upper bound in such plots that represented the state-of-the-art performance against which the gas permeability data of new polymers could be compared (L. M. Robeson ". o., 1991). The originally published data for PIM1 and PIM-7 were well above the 1991 upper bound for important gas pairs such as O2/N2 and CO2/CH4 (P. M. Budd K. J., 2005). This data contributed to Robeson's revision of the upper boundsin 2008 (L. M. Robeson, 2008). Subsequently, it was found that the permeability of PIM-1 could be enhanced further by the simple treatment of solvent cast films by methanol, which helps flush out residual solvent and allows relaxation of the polymer chains (P. M. Budd N. B., 2008)[103]. Methanol-treated PIM-1 provides data just above the 2008 upper bounds for the CO2/N2 and CO2/CH4 gas pairs (P. M. Budd N. B., 2008). In common with other glassy polymers, the transport properties of PIMs are strongly dependent on their processing history. This accounts for the large variation in reported gas permeation data for PIM-1 [ (C. L. Staiger, 2008), (P. M. Budd N. B., 2008), (S. Thomas, 2009). In particular, residual solvent from casting and ageing of films, the latter a phenomenon shown by all glassy polymers especially those with high free volume (K. D. Dorkenoo and P. H. Pfromm, 2000), cause a reduction in permeability. Therefore, in order to allowa fair comparison between PIMs, it is best to use methanol treatment of the polymer film to ensureremoval of casting solvent and to "reset" the ageing clock.





## Figure 9:

Robeson plots for (a)  $O_2/N_2$ , (b)  $CO_2/N_2$ , (c)  $CO_2/CH_4$ , and (d)  $H_2/N_2$  gas pairs showing the data for PIMs. The black and red lines represent the 1991 and 2008 upper bounds, respectively. References for notable data points are given in square brackets. Data for methanol treated films of PIM-1 are given as green squares whereas the data for a methanol treated film of spirobisfluorene-based PIM, prepared from monomer **A18**, is given as a red square.Data for other PIMs are given as black triangles and for PIM polyimides as black circles.

PIMs have been found as novel membranes for separating many organic compounds via the pervaporation process (Kirk et al., 2019). PIMs have also been utilized as effective heterogeneous catalysis as they have many catalytic sites (Kaur et al., 2011, McKeown and Budd, 2006). Moreover, PIMs have been successfully utilized applications towards sensors ongoing to their efficient properties, including unique optical fluorescence and intrinsic microporosity. Thus, many organic vaporous and explosive chemicals could be selectively detected with a low level through the use of PIM-1 as optical sensors and light-emitters (Carturan et al., 2010, Rakow et al., 2010, Thomas et al., 2011). PIMs have been additionally found as a gas storage medium (McKeown andBudd, 2006). Furthermore, many studies have been documented on the uses of PIMs as effective synthetic adsorbents for the treatment of harmful chemical/pollutants in aqueous systems and realsamples (Budd et al., 2003, McKeown and Budd, 2006).

## 4.1.4. Wastewater Treatment and Removal of Harmful Pollutants

Freshwater has a vital and essential role in our planet and for human health (Elimelech, 2006, Kumar and Puri, 2012). Nowadays, one of the most common problems faced by humans over the world is water contamination. Pollutants by Human-made activities can come from various ways, including industrial effluents, agricultural products or by-products, wrong disposing or storing of domestic chemical products like detergents, and several chemical solvents (Al Yaqout, 2003, Jegatheesan et al., 2011, Kass et al., 2005). Environmental pollutants such as inorganic, organic, radiological, and biological contaminants are mainly categorized as the most common types of contaminants related to water, soil, and air pollution (Sharma and Bhattacharya, 2017).

In the last three decades, several techniques, including adsorption, advanced oxidation processes, coagulation, filtration with coagulation, ion exchange, ozonation, precipitation, and reverse osmosis, have

been commonly used to remove chemical pollutants from wastewater and polluted water (Elwakeel et al., 2020). Among the possible techniques, adsorbents' use via the adsorption method has been selected to be superior to other methods (Alnajrani and Alsager, 2020, Budd et al., 2005, Satilmis, 2020). It is introduced as an effective separation process for water treatment due to its designable, operatable, flexibility, low cost, and tactlessness to harmful pollutants (Rashed, 2013, Taghizade Firozjaee et al., 2018). In recent years, synthetic adsorbents such as PIMs have been efficiently applied to remove various chemical pollutants in the environment (Ye et al., 2020). Among them includes heavy metals (Zhang et al., 2016b), dyes (Satilmis, 2020), pharmaceutical-emerging contaminants (Alnajrani and Alsager, 2020), and other organic pollutants(Budd et al., 2003) in water/wastewater. The capacity and efficiency of PIMs towards the removal of harmful chemicals in environmental samples have been documented in many previous studies (Table 1).

PIMs (Adsorbent) PIM-1 (Dense film)	BET specific surface area (m²/g ) 976	Pollutants Classificati Dyes	on	Pollutants (Adsorbates) Solvent Blue 35	рН -	Contact time min(h) 200	Capacity (mg/L) 41.548	References
				Oil Red O	-	200	65.501	(Zhang et
(PIM-1) fibers (F10) (electrospun	1114	Dyes		Solvent Blue 35 Oil Bod O	-	20	42.122	al., 2016a)
fiber)					-	20	00.807	
AmidoximePIM- 1 Hydrolysed PIM-1 fibers	550	Dyes		Methylene Blue	6	180	69.8	(Satilmis, 2020)
				Methyl Orange	6	180	79.8	
				Methyl orange	7	300	42.38	
	нтом	Dyes		Methylene blue	7	300	424.80	(Zhang et al., 2016b)
				Methylene violet	7	300	317.26	
				Safranin O	7	300	364.29	
Amidoxime- PIM	531	Heavy ion	metals	Uranyl [U(VI)]	6	(6)	41	(Sihn et al. <i>,</i> 2016)
Hydrolysed	нтом	Heavy	metals	Pb(II)	5	300	41.2	(Zhang et
PIM-1 fibers		ion		Cu(II)	6	300	16.9	al. <i>,</i> 2016b)
PIM-1	630	pharmaceutical- emerging contaminants or antibiotics		Doxycycline	7	(5)	178.60	(Alnajrani and Alsager, 2020)
				Ciprofloxacin	2	(5)	31.15	
				Penicillin G	2	(24)	191.04	
				Amoxicillin	2	(24)	208.60	
Crosslinked PIMs	775	Other pollu	itants	Phenol	6— 7	overnight	470	(Budd et al., 2003)

Table 1: shows detailed information on the proposed PIMs for remediation of waters from chemical pollutants

HTOM; higher than original material (PIM-1), BET; Brunauer-Emmett-Teller, h; the hour,

The obtained results from previous studies (Table 1) showed that the PIMs materials had been effectively applied for the water treatment in terms of chemical pollutants. Among them includes dyes, heavy metals, pharmaceutical products, and other toxic pollutants. Results verified that PIMs materials have different capacities for the adsorption of toxic dyes in real environmental samples. Results also confirmed that the modification of PIMs-1 with various constituents could cause a change in their capacity to remove the same pollutants.

#### 4.2. Sensors

The combination of solution processability, porosity, and optical clarity makes PIMs useful for sensor applications. For example, the incorporation of the fluorescent dye Nile Red into solvent cast films of PIM-3 (formed from monomers **A1** and **B3**, see Table <u>1</u>) produced an optical sensor for ethanol (S. Carturan A. A., 2010), (S. Carturan A. A., 2008). The intrinsic fluorescence of PIM-1 has also been exploited in sensors described in patents and enabled the fabrication of a laser sensor with great sensitivity for the detection of nitrated aromatics (Y. Wang, 2011). A colorimetricoptical sensor based on the rapid change in refractive index of a thin film of PIM-1 on adsorption of organic vapor provides a dramatic green-to-red color change, which can be visualised for sensingconcentrations in air down to 50 ppm or, if using a fibre-optic spectrometer, down to 50 ppb (J. C.Thomas, 2011), (N. A. Rakow, 2010.).

The optical response is general for all organic vapors but the hydrophobic nature of PIM-1ensures the lack of interference by humidity. The fabrication and performance of this device both benefit from the unique combination of solvent processability and microporosity of the PIM component. In sensor application, PIM-1 has been used as a medium for adsorbing organics from air which can then be desorbed by heating into a conventional sensor [ (D. J. Combes, 2012), (S.T. Hobson, 2012.). For this application, the thermal stability of PIMs is of importance. The ease of use, applicability, and high permeability of the PIM-GO modified with graphene oxide (GO), which strengthens the mechanical structure, and permeability of PIMs at high temperatures afford significant advantages over the unmodified membranes. The results of this development can aid significantly of next-generation membranes with increased mechanical stability, to be used as membranes in industrial applications. The high transport efficiency of the PIM-GO at temperatures exceeding room temperature is evidence of the improved thermal stability of the PIM-GO. (CananOnac1, 2020)

## 5. Conclusion and summary:

In this review we demonstrated the brief review on aspects polymers intrinsic microporosity PIMs which was discovered by scientist for nearly 20 years. This review focuses on the available and applied methods to synthesis polymers with microporosity. Among them include polymers that poses microporosity, such as polymers of intrinsic microporosity (PIMs). PIM may be prepared either as insoluble or soluble polymers, with both types exhibiting typical microporous materials behaviors.

We reviewed about the methods could be readily utilized for the formation of different PIMs with their various novel properties. Synthetic methods related to PIMs have been recently enhanced to develop their adequate properties. The ease of making PIM-1 from commercial starting materials also allows groups with only limited expertise in polymer synthesis to engage in research to fully explore the properties and applications of this material. Many potential applications of several PIMs materials have been found owing to their potential active surface area and high rigidity. ThePIMs can be applied with high capacity as an alternative to other synthetic adsorbents in variety of applications. The intense activity on PIMs for gas separations should result in better materials and optimized membrane fabrication in future. In our opinion, the most challenging task for the successful transition of PIM- or PIM–PI-based membranes to industrial applications requires improvements in their membrane stability. As high-free-volume polymers exist in a nonequilibrium state, their gas permeation properties are dynamic in nature and can change over extended periods of time. In fact, the extremely thickness-dependent physical aging behavior of high-free-volume PIMs makes it difficult to assign "intrinsic" gas permeation properties to a given polymer. Future research needs to include more

detailed studies on thin films (<1  $\mu$ m) as they represent a more realistic physical state of the PIM material applied as membrane rather than only relying on bulk, thick-film data (typically > 50  $\mu$ m).

Finally, in this review we provide a brief summary on the potential use of PIM-derived membrane materials for the areas of nanofiltration. In summary, we conclude that successful development of high-performance membranes for industrial applications requires demonstration of the categories such as: a) Materials development, b) Structural materials design and small-scale synthesis; c) materials characterization—solubility, thermal, and mechanical properties; d) intrinsic, materials permeation properties—pure and mixture permeability; e) component selectivity; and f) long-term stability of transport properties, such as stability of membrane properties under high-pressure conditions. Materials and membrane scale-up which include material synthesis scale-up for commercial membrane production, and reproducible and cost-effective membrane scale- production, depending on applications. Many research organisations are now engaged on research involving PIMs both in industry and academia so that the rate of progress is likely to increase further in coming future.

#### 6. References

- 1. Al yaqout, A. F. 2003. Assessment and analysis of industrial liquid waste and sludgedisposal at unlined landfill sites in arid climate. *Waste Management*, 23, 817-824.
- 2. Alnajrani, M. N. & Alasger O. A. 2020. Removal of Antibiotics from Water by polymerof intrinsic microporosity: isotherms, Kinetics, thermodynamics, and Adsorption Mechanism. *Scientific Reports*, 10, 1-14.
- 3. Adymkanov S. V., Yampol'skii Y. P., Polyakov A. M. et al., 2008, "Pervaporation of alcohols through highly permeable PIM-1 polymer films," Polymer Science A, vol. 50, no.4, pp. 444–450.
- Ahn J., Chung W. J., Pinnau I. et al., 2010, "Gas transport behavior of mixed-matrixmembranes composed of silica nanoparticles in a polymer of intrinsic microporosity(PIM1)," Journal of Membrane Science, vol. 346, no. 2, pp. 280–287.
- Bezzu, C. G., Carta, M., Tonkins, A., Jansen, J. C., Bernardo, P., Bazzarelli, F. & MckeownN, N. B. 2012. A spirobifluorene-based polymer of intrinsic microporosity with improved performance for gas separation. *Advanced Materials*, 24, 5930-5933.
- Budd, P. M., Elabas, E. S., Ghanem, B. S., Makhseed, S., Mckeown, N. B., Msayib K. J., Tattershall, C. E. & Wang, D. 2004a. Solution-processed, organophilic membrane derived from a polymer of intrinsic microporosity. *Advanced Materials*, 16, 456-459.
- 7. Bubb, P. M., Ghanem, B., Msayib, K., Mckeown, N. B. & Tattershall, C. 2003. A nanoporous network polymer derived from hexaazatrinaphthylene with potential as anadsorbent and catalyst support. *Journal of Materials Chemistry*, 13, 2721-2726.
- 8. Budd, P. M., Ghanem, B. S., Makhseed, S., Mckeown, N. B., Msayib, K. J. & Tattershall, C. E. 2004b. Polymers of intrinsic microporosity (PIMs): robust, solution-processable, organic nanoporous materials. *Chemical communications*, 230-231.
- 9. Budd, P. M., Msayib, K. J., Tattershall, C. E., Ghanem, B. S., Reynolds, K. J., Mckeown,
- N. B. & Fritsch, D. 2005. Gas separation membranes from polymers of intrinsic microporosity. *Journal of Membrane Science*, 251, 263-269.
- 10. Bernardo P.; E. Drioli; G. Golemme,2009, Membrane Gas Separation: A Review/State of the Art. Industrial & Engineering Chemistry Research. 48(10), 4638 (2009).
- 11. Brunauer S., Emmett P. H., and Teller E., 1938, "Adsorption of gases in multimolecular layers," Journal of the American Chemical Society, vol. 60, no. 2, pp. 309–319.
- 12. Bezzu C. G., Carta M., Tonkins A. et al., "A spirobifluorenebased polymerof intrinsic microporosity with improved performance for gas separations," Advanced Materials. Inpress.
- Budd P. M., McKeown N. B., Ghanem B. S. et al., 2008, "Gas permeation parameters and other physicochemical properties of apolymer of intrinsic microporosity: polybenzodioxane PIM1," Journal of Membrane Science, vol. 325, no. 2, pp. 851–860.
- 14. Bernardo P., Drioli E., and Golemme G., 2009, "Membrane gas separation: a review/stateof the art," Industrial and Engineering Chemistry Research, vol. 48, no. 10, pp. 4638–4663.
- 15. Baker R. W., 2002, "Future directions of membrane gas separation technology," Industrial and Engineering

Chemistry Research, vol. 41, no. 6, pp. 1393–1411.

- 16. Budd P. M., Msayib K. J., Tattershall C. E. et al.,2005, "Gas separation membranes from polymers of intrinsic microporosity," Journal of Membrane Science, vol. 251, no. 1-2, pp.263–269.
- 17. Canan Onac1, Ahmet Kaya1, Necip Atar2, Izzet Sener3 and Hamza Korkmaz Alpoguz (2020), "Superiority of Modified Polymeric Membrane with Nanomaterial on Temperatureand Mechanical Stability and Application in Industrial Waste Water"
- Carta M., Msayib K. J., and McKeown N. B., 2009, "Novel polymers of intrinsic microporosity (PIMs) derived from 1,1- spiro-bis(1,2,3,4-tetrahydronaphthalene)-basedmonomers,"Tetrahedron Letters, vol. 50, no. 43, pp. 5954–5957.
- 19. Carta M., Msayib K. J., Budd P. M., and McKeown N. B., 2008, "Novel spirobisindanes for use as precursors to polymers of intrinsic microporosity," Organic Letters, vol. 10, no.13, pp. 2641–2643
- Carturan S., Antonaci,A. Quaranta A. et al., 2010, "Optical sensing capabilities of polymers of intrinsic microporosity (PIMs)," in Sensors and Microsystems: AISEM 2009Proceedings, P. Malcovati, A. Baschirotto, A. d'Amico, and C. Natale, Eds., pp. 55–58, Springer, New York, NY, USA.
- Carturan S., Antonaci A., Quaranta A. et al., 2010, "Optical sensing capabilities of polymers of intrinsic microporosity (PIMs)," in Sensors and Microsystems: AISEM 2009Proceedings, P. Malcovati, A. Baschirotto, A. d'Amico, and C. Natale, Eds., pp. 55–58, Springer, New York, NY, USA.
- 22. Carturan S., Antonaci1A., Quaranta A. et al., 2008, "Optical vapor sensing capabilities of polymers of intrinsic microporosity (PIMs)," LNL Annual Report, Applied and Interdisciplinary Physics 100-101.
- 23. Combes D. J., Cox T. I., and Sage I. C. , 2012, "Preconcentrator device," US 08137979.
- 24. Dawson R., Cooper, A. I. and Adams D. J., (2012) "Nanoporous organic polymernetworks," Progress in Polymer Science, vol. 37, no. 4, pp. 530–563.
- 25. Dorkenoo K. D. and Pfromm P. H., 2000, "Accelerated physical aging of thin poly[1-(trimethylsilyl)-1-propyne] films," Macromolecules, vol. 33, no. 10, pp. 3747–3751.
- Du N. Y., Robertson G. P., Pinnau I., Thomas S., and Guiver M. D., 2009, "Copolymers of Intrinsic Microporosity Based on 2,2,3,3- Tetrahydroxy-1,1-dinaphthyl," Macromolecular Rapid Communications, vol. 30, no. 8, pp. 584–588.
- 27. Du N. Y., Robertson G. P., Pinnau I., and Guiver M. D., 2010, "Polymers of intrinsic microporosity with dinaphthyl and thianthrene segments," Macromolecules, vol. 43, no.20, pp.8580–8587.
- 28. Du N. Y., Guiver M. D., and Gilles R. P., 2011, "Ladder polymers with instrinsic microporosity and process for production thereof," US, 0190409 A1.
- 29. Du N. Y., Robertson, Pinnau G. P. I., and Guiver M. D. , 2009, "Polymers of intrinsic microporosity derived from novel disulfone-based monomers," Macromolecules, vol. 42,no. 16,pp. 6023–6030.
- Du N. Y., Robertso G. P. n, Song J. Pinnau, I., Thomas S., andGuive M. D. r, 2008, "Polymers of intrinsic microporosity containing trifluoromethyl and phenylsulfone groups as materials for membrane gas separation," Macromolecules, vol. 41, no. 24, pp. 9656–9662.
- 31. Du N. Y., Robertson G. P., Pinnau I., and Guiver M. D., 2010, "Polymers of intrinsic microporosity with dinaphthyl and thianthrene segments," Macromolecules, vol. 43, no.20, pp. 8580–8587.
- 32. Du N. Y., Park H. B., Dal-Cin M. M., and Guiver M. D., 2012, "Advances in high permeability polymeric membrane materials for CO2 separations," Energy & Environmental Science, vol. 5, no. 6, pp. 7306–7322.
- Du N. Y., M. Cin M. D., Pinnau I., Nicalek A., Robertson G. P., and Guiver M. D., 2011, "Azide-based crosslinking of polymers of intrinsic microporosity (PIMs) for condensable gas separation," Macromolecular Rapid Communications, vol. 32, no. 8, pp. 631–636.
- 34. Emmler T., Heinrich, K. Fritsch D. et al., 2010, "Free volume investigation of polymers of intrinsic microporosity (PIMs): PIM1 and PIM1 copolymers incorporating ethanoanthracene units," Macromolecules, vol. 43, no. 14, pp. 6075–6084.
- 35. Fang W., Zhang L., and Jiang J., 2010, "Polymers of intrinsic microporosity for gas permeation: a molecular simulation study," Molecular Simulation, vol. 36, no. 12, pp.992–1003.
- Carta, M., Croad, M., Malpas-Evans, R., Jansen, J. C., Bernardo, P., Clarizia, G., Friess, K., Lanc', M. & Mckeown, N. B. 2014a. Triptycene induced enhancement of membrane gas selectivity for microporous Tröger's base polymers. *Advanced Materials*, 26, 3526-3531.
- 37. Carta, M., Malpass-Evans, R., Croad, M., Rogan, Y., Lee, M., Rose, I. & Mckeown, N. B.2014b. The synthesis of

microporous polymers using Tröger's base formation. Polymer Chemistry, 5, 5267-5272.

- 38. Carturan, S., Antonaci, A., Maggioni, G., Quaranta, A., Tonezzer, M., Milan, R. & Dellamea, G. 2010. Optical vapors sensing capabilities of polymers of intrinsic microporosity. *Sensors and Microsystems*. Springer.
- 39. Doble, M. 2007. Perry's chemical engineers' handbook. McGraw-Hill, New York, USA.
- 40. Du, N., Robertson, G. P., Song, J., Pinnau, I. & Guiver, M. D. 2009. High-performancecarboxylated polymers of intrinsic microporosity (PIMs) with tunable gas transport properties. *Macromolecules*, 42, 6038-6043.
- 41. Du, N., Robertson, G. P., Song, J., Pinnau, I., Thomas, S. & Guiver, M. D. 2008. Polymers of intrinsic microporosity containing trifluoromethyl and phenylsulfone groups as materials for membrane gas separation. *Macromolecules*, 41, 9656-9662.
- De Miranda R. L., Kruse J., Ratzke K. et al., 2007, "Unusual tem- "perature dependence of the positron lifetime in a polymer of intrinsic microporosity," Physica Status Solidi-Rapid Research Letetrs, vol. 1, no. 5, pp. 190–192. on membrane structure and gas permeation ina polymer of intrinsic microporosity: insight from atomistic simulation,"Journal of Physical Chemistry C, vol. 115, no. 22, pp. 11233–11239.
- 43. Eastmond, G. C., Paprotny, J., Steiner, A. & Swanson, L. 2001. Synthesis of cyanodibenzo [1, 4] dioxines and their derivatives by cyano-activated fluoro displacement reactions. *NewJournal of Chemistry*, 25, 379-384.
- 44. Elimelech, M. 2006. The global challenge for adequate and safe water. *Journal of WaterSupply: Research and Technology—AQUA*, 55, 3-10.
- 45. Elwakeel, K. Z., Elgarahy, A. M., Khan, Z. A., Almughamisi, M. S. & Al-Bogami, A. S. 2020. Perspectives regarding metal/mineral-incorporating materials for water purification: with special focus on Cr(VI) removal. *Materials Advances*, 1, 1546-1574.
- 46. Fawell, J. & Nieuwenhuijsen, M. J. 2003. Contaminants in drinking waterEnvironmental pollution and health. *British medical bulletin*, 68, 199-208.
- 47. Fang W., Zhang L., and Jiang J., 2011, "Gas permeation and separation in functionalized polymers of intrinsic microporosity: a combination of molecular simulations and ab initio calculations," Journal of Physical Chemistry C, vol. 115, no. 29, pp. 14123–14130.
- 48. Freeman B. D., 1999, "Basis of permeability/selectivity tradeoff relations in polymeric gas separation membranes," Macromolecules, vol. 32, no. 2, pp. 375–380.
- Fritsch D., Bengtson G., Carta M., and McKeown N. B., 2011, "Synthesis and gas permeation properties, ISRN Materials Science 15 of spirobischromane-based polymers of intrinsic microporosity," Macromolecular Chemistry and Physics, vol. 212, no. 11, pp. 1137–1146.
- 50. Fritsch D., Merten P., Heinrich K., Lazar M., and Priske M., 2012 "High performance organic solvent nanofiltration membranes: development and thorough testing of thin film composite membranes made of polymers of intrinsic microporosity (PIMs)," Journal of Membrane Science, vol. 401, pp. 222–231.
- 51. Ghanem B. S., McKeown N. B., Budd P. M., Selbie J. D., and Fritsch D. , 2008, "High-performance membranes from polyimides with intrinsic microporosity," Advanced Materials, vol. 20, no. 14, pp. 2766–2771.
- 52. Ghanem B. S., McKeown N. B., Budd P. M. et al., 2009, "Synthesis, characterization, and gas permeation properties of a novel group of polymers with intrinsic microporosity: PIMpolyimides," Macromolecules, vol. 42, no. 20, pp. 7881–7888.
- 53. Han S. H., Lee J. E., Lee K. J., Park H. B., and Lee Y. M., 2010, "Highly gas permeable and microporous polybenzimidazole membrane by thermal rearrangement," Journal of Membrane Science, vol. 357, no. 1-2, pp. 143–151.
- Han S. H., Misdan N., Kim S., Doherty C. M., Hill A. J., and Lee Y. M., 2010, "Thermally rearranged (TR) polybenzoxazole: effects of diverse imidization routes on physical properties and gas transport behaviors," Macromolecules, vol. 43, no. 18, pp. 7657–7667.
- 55. Harms S., Ratzk K. e, Faupel F. et al., 2012, "Aging and free volume in a polymer of intrinsic microporosity (PIM-1)," Journal of Adhesion, vol. 88, no. 7, pp. 608–619.
- Heuchel M., Fritsch D., Budd P. M., McKeown N. B., and Hofmann D., 2008, "Atomisticpacking model and free volume distribution of a polymer with intrinsic microporosity (PIM1)," Journal of Membrane Science, vol. 318, no. 1-2, pp. 84–99.
- 57. Hobson S. T., Cemalovic S., and Patel S. V., 2012, "Preconcentration and detection of chlorinated organic compounds and benzene," Analyst, vol. 137, no. 5, pp. 1284–1289.
- 58. Horvath G. and Kawazoe K., 1983, "Method for the calculation of effective pore-size distribution in molecular-

sieve carbon," Journal of Chemical Engineering of Japan, vol.16, no. 6, pp. 470–475.

- Ghanem, B. S., Mckeown, N. B., Budd, P. M., Al-Harbi, N. M., Fritsch, D., Heinrich, K., Starnnikova, L., Tokarev, A. & Yampoliskii, Y. 2009. Synthesis, characterization, and gas permeation properties of a novel group of polymers with intrinsic microporosity: PIM- polyimides. *Macromolecules*, 42, 7881-7888.
- 60. Ghanem, B. S., Mckeown, N. B., Budd, P. M., Selbie, J. D. & Fritsch, D. 2008. High-performance membranes from polyimides with intrinsic microporosity. *Advanced Materials*, 20, 2766-2771.
- 61. Heuchel, M., Fritsch, D., Budd, P. M., Mckeown, N. B. & Hofmann, D. 2008. Atomisticpacking model and free volume distribution of a polymer with intrinsic microporosity (PIM-1). *Journal of Membrane Science*, 318, 84-99.
- 62. Ilinitch O. M., Fenelonov V. B., Lapkin A. Okkel A., L. G., Terskikh V. V., and Zamaraev,K. I. (1999) "Intrinsic microporosity and gas transport in polyphenylene oxide polymers," Microporous and Mesoporous Materials, vol. 31, no. 1-2, pp. 97–110.
- 63. Jegatheesan, V., Shu, L. & Visvanathan, C. 2011. Aquaculture effluent: impacts and remedies for protecting the environment and human health. *Encyclopedia of environmentalhealth*, 123-135.
- 64. Kass, A., Gavrieli, I., Yechieli, Y., Vengosh, A. & Starinsky, A. 2005. The impact of freshwater and wastewater irrigation on the chemistry of shallow groundwater: a case study from the Israeli Coastal Aquifer. *Journal of Hydrology*, 300, 314-331.
- 65. Kaur, P., Hupp, J. T. & Nguyen, S. T. 2011. Porous organic polymers in catalysis:opportunities and challenges. *ACS Catalysis*, 1, 819-835.
- 66. Kirk, R. A., Putintseva, M., Volkov, A. & Budd, P. M. 2019. The potential of polymers of intrinsic microporosity (PIMs) and PIM/graphene composites for pervaporation membranes. *BMC Chemical Engineering*, **1**, 18.
- 67. Kricheldorf, H. R., Fritsch, D., Vakhtangishvilli, L. & Schwarz, G. 2005. Cyclic Ladder Polymers by Polycondensation of Silylated Tetrahydroxy-tetramethylspirobisindane with 1, 4-Dicyanotetrafluorobenzene. *Macromolecular Chemistry and Physics*, 206, 2239-2247.
- 68. Kumar, M. & Puri, A. 2012. A review of permissible limits of drinking water. *Indianjournal of occupational and environmental medicine*, 16, 40.
- 69. Larsen G. S., Lin P., Siperstein F. R., and Colina C. M., 2011, "Methane adsorption inPIM-1," Adsorption, vol. 17, no. 1, pp. 21–26.
- 70. Larsen G. S., Lin P., Hart K. E., and Colina C. M., 2011, "Molecular simulations of PIM-1-like polymers of intrinsic microporosity," Macromolecules, vol. 44, no. 17, pp. 6944– 6951.
- 71. Liu C. S., Kulprathipanja S., and Wilson S. T., 2007, "High flux mixed matrix membranesfor separations," United States, 0209505.
- 72. Liu C. S., Faheem S. A., and Minkov R., 2012, "Membrane system for natural gas upgrading," United States, 20120157743.
- 73. Li F. Y., Xiao Y., Chung T. S., and Kawi S., 2012, "High-performance thermally self-cross-linked polymer of intrinsic microporosity (PIM-1): membranes for energy development," Macromolecules, vol. 45, no. 3, pp. 1427–1437.
- Liu C., Wilson S. T., and Lesch D. A., 2010, "UV-cross-linked membranes from PIMs for liquid separation," US 7758751.McKeown N. B. and Budd P. M., (2010), "Exploitation of intrinsic microporosity in polymer-based materials," Macromolecules, vol. 43, no. 12, pp. 5163–5176,
- 75. Luis P., Gerven T. van, and Bruggen B. van der, 2012, "Recent developments in membrane-based technologies for CO2 capture," Progress in Energy and CombustionScience, vol. 38, no. 3, pp. 419–448.
- 76. Lee, M., Bezzu, C. G., Carta, M., Bernardo, P., Clarizia, G., Jansen, J. C. & Mckeown, N. B. 2016. Enhancing the gas permeability of Troger's base derived polyimides of intrinsic microporosity. *Macromolecules*, 49, 4147-4154.
- 77. Ma, X., Salinas, O., Litwiller, E. & Pinnau, I. 2013. Novel spirobifluorene-and dibromospirobifluorene-based polyimides of intrinsic microporosity for gas separationapplications. *Macromolecules*, 46, 9618-9624.
- 78. Makhseed, S., Ibrahim, F. & SAMUEL, J. 2012. Phthalimide based polymers of intrinsic microporosity. *Polymer*, 53, 2964-2972.
- 79. Marken, F., Carta, M. & Mckeown, N. B. 2020. Polymers of Intrinsic Microporosity in the Design of Electrochemical Multicomponent and Multiphase Interfaces. ACS Publications.
- 80. Mckeown, N. B. 2012. Polymers of intrinsic microporosity. *ISRN Materials Science*, 2012.

- 81. Mckeown , N. B. 2017. The synthesis of polymers of intrinsic microporosity (PIMs). *Science China Chemistry*, 60, 1023-1032.
- 82. McKeown Neil B, (2012) Polymers of Intrinsic Microporosity. ISRN Materials Science. 2012, 1.
- 83. McKeown N. B., (1998), Phthalocyanine Materials: Synthesis, Structure and Function, CUP, Cambridge, UK,.
- 84. Mckeown , N. B. & Budd, P. M. 2006. Polymers of intrinsic microporosity (PIMs): organic materials for membrane separations, heterogeneous catalysis and hydrogenstorage. *Chemical Society Reviews*, 35, 675-683.
- 85. Mohan, D. & Pittman, JR., C. U. 2007. Arsenic removal from water/wastewater using adsorbents—a critical review. *Journal of hazardous materials*, 142, 1-53.
- 86. McKeown N. B. and Budd P. M., (2009), "Polymers of intrinsic microporosity," in Encyclopedia of Polymer Science and Technology, John Wiley & Sons, New York, NY,USA,.
- 87. Makhseed S., . Ibrahim F, and SamueJ. L.,2012, "Phthalimide based polymers of intrinsic microporosity," Polymer, vol. 53, no. 14, pp. 2964–2972.
- 88. Ma X. H., Swaidan R., Belmabkhout Y. et al., 2012, "Synthesis and gas transport properties of hydroxylfunctionalized polyimides with intrinsic microporosity," Macromolecules, vol. 45, no. 9, pp. 3841–3849.
- McKeown N. B., Li H., and Makhseed S., (2001) "Towards phthalocyanine network polymers for heterogeneous catalysis," in Supported Catalysts and Their Applications, D. C. Sherrington and A. P. Kybett, Eds., pp. 214–217, RSC Publishing, Cambridge, UK,.
- McDermott A.G., Larsen G. S., Budd P. M., Colina C. M., and Runt J., 2011, "Structural characterization of a polymer of intrinsic microporosity: X-ray scattering with interpretation enhanced by molecular dynamics simulations," Macromolecules, vol. 44, no.1, pp. 14–16.
- 91. Park H. B., Jung C. H., Lee Y. M. et al., 2007, "Polymers with cavities tuned for fast selective transport of small molecules and ions," Science, vol. 318, no. 5848, pp. 254–258.
- 92. Park H. B., Han S. H., Jung C. H., Lee Y. M., and Hill A. J., 2010, "Thermally rearranged(TR) polymer membranes for CO2 separation," Journal of Membrane Science, vol. 359, no. 1-2, pp. 11–24.
- 93. Priske M., Baumgarten G., H. G. Lueken et al., 2012, "Method for enriching a homogeneous catalyst from a process flow," US 0046503 A1, 16 ISRN Materials Science.
- Rakow, N. A., Wendland, M. S., Trend, J. E., Poirier, R. J., Paolucci, D. M., Maki, S. P., Lyons, C. S. & Swierczek, M. J. 2010. Visual indicator for trace organic volatiles. *Langmuir*, 26, 3767-3770.
- 95. Rashed, M. N. 2013. Adsorption technique for the removal of organic pollutants fromwater and wastewater. *Organic pollutants-monitoring, risk and treatment,* 167-194.
- Rogan, Y., Malpass-Evans, R., Carta, M., Lee, M., Jansen, J. C., Bernardo, P., Clarizia, G., Tocci, E., Friess, K. & Lanc<sup>^</sup>, M. 2014. A highly permeable polyimide with enhanced selectivity for membrane gas separations. *Journal of Materials Chemistry A*, 2, 4874-4877.
- 97. Rakow N. A., Wendland M. S., Trend J. E. et al., 2010, "Visual indicator for trace organicvolatiles," Langmuir, vol. 26, no. 6, pp. 3767–3770.
- 98. Robeson L. M., 1991, "Correlation of separation factor versus permeability for polymericmembranes," Journal of Membrane Science, vol. 62, no. 2, pp. 165–185.
- Robeson L. M., 2008, "The upper bound revisited," Journal of Membrane Science, vol. 320, no. 1-2, pp. 390–400.
- Robeson L. M., Freeman B. D. D., Paul R., and Rowe B. W., 2009, "An empirical correlation of gas permeability andpermselectivity in polymers and its theoretical basis," Journal of Membrane Science, vol. 341, no. 1-2, pp. 178–185.
- 101. Scholes C. A., Stevens G. W., and Kentish S. E., 2012, "Membrane gas separation applications in natural gas processing," Fuel, vol. 96, no. 1, pp. 15–28.
- 102. Satilmis, B. 2020. Amidoxime Modified Polymers of Intrinsic Microporosity (PIM-1); AVersatile Adsorbent for Efficient Removal of Charged Dyes; Equilibrium, Kinetic and Thermodynamic Studies. *Journal of Polymers and the Environment*, 28, 995-1009.
- 103. Sharma, S. & Bhattacharya, A. 2017. Drinking water contamination and treatment techniques. *Applied Water Science*, 7, 1043-1067.
- 104. Shaver, M. P. 2014. Book review: Encyclopedia of Polymer Science and Technology. Thomas Telford Ltd.
- 105. Sihn, Y. H., Byun, J., Patel, H. A., Lee, W. & Yavuz, C. T. 2016. Rapid extraction of uranium ions from seawater using novel porous polymeric adsorbents. *RSC advances*, 6,45968-45976.

- 106. Sing, K. S. 1985. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity (Recommendations 1984). *Pureand applied chemistry*, 57, 603-619.
- 107. Staiger, C. L., Pas, S. J., Hill, A. J. & Corrnelius, C. J. 2008. Gas separation, free volume distribution, and physical aging of a highly microporous spirobisindane polymer. *Chemistry of Materials*, 20, 2606-2608.
- 108. Swaidan, R., Al-Saeedi, M., Ghanem, B., Litwiller, E. & Pinnau, I. 2014. Rational design of intrinsically ultramicroporous polyimides containing bridgehead-substituted triptycene for highly selective and permeable gas separation membranes. *Macromolecules*, 47, 5104-5114.
- 109. Song J., Du N. Y., Dai Y. et al., 2008, "Linear high molecular weight ladder polymers by optimized polycondensation of tetrahydroxytetramethylspirobisindane and 1,4- dicyanotetrafluorobenzene," Macromolecules, vol. 41, no. 20, pp. 7411–7417.
- 110. Staiger C. L., Pas S. J., Hill A. J., and Cornelius C. J., 2008, "Gas separation, free volume distribution, and physical aging of a highly microporous spirobisindane polymer," Chemistry of Materials, vol. 20, no. 8, pp. 2606–2608.
- 111. Short R., Carta M., C. Bezzu G., Fritsch D., B. Kariuki M., and McKeown N. B., 2011"Hexaphenylbenzene-based polymers of intrinsic microporosity," Chemical Communications, vol. 47, no. 24, pp. 6822–6824,.
- 112. Thomas S., I. Pinnau, Du N. Y., and Guiver M. D., 2009, "Pureand mixed-gas permeation properties of a microporous spirobisindane-based ladder polymer (PIM-1)," Journal of Membrane Science, vol. 333, no. 1-2, pp. 125–131.
- Tao S. J., 1972, "Positronium annihilation in molecular substances," The Journal of Chemical Physics, vol. 56, no. 11, pp. 5499– 5510.
- 114. Thomas S., Pinnau I., Du N. Y., and Guiver M. D., 2009, "Hydrocarbon/hydrogen mixed-gas permeation properties of PIM1, an amorphous microporous spirobisindane polymer," Journal of Membrane Science, vol. 338, no. 1-2, pp. 1–4.
- 115. Thomas J. C., Trend J. E., Rakow N. A., Wendland M. S., Poirier R. J., and Paolucci D.M., 2011, "Optical sensor for diverse organic vapors at ppm concentration ranges," Sensors, vol. 11, no. 3, pp. 3267–3280.
- 116. Taghizade Firozjaee, T., Mehradi, N., Baghdadi, M. & Nabi Bidhendi, G. 2018. Application of nanotechnology in pesticides removal from aqueous solutions-a review. *International Journal of Nanoscience and Nanotechnology*, 14, 43-56.
- 117. Tao, S. 1972. Positronium annihilation in molecular substances. The Journal of ChemicalPhysics, 56, 5499 5510.
- 118. Thomas, J. C., Trend, J. E., Rakow, N. A., Wedland, M. S., Poirier, R. J. & Paolucci, D. M. 2011. Optical sensor for diverse organic vapors at ppm concentration ranges. *Sensors*, 11, 3267-3280.
- 119. Vandezande P., Gevers L. E. M., and Vankelecom I. F. J., 2008, "Solvent resistant nanofiltration: separating on a molecular level," Chemical Society Reviews, vol. 37, no. 2,pp. 365–405.
- 120. Wang Y., McKeown N. B., Msayib K. J., Turnbull G. A., and Samuel I. D. W., 2011, "Laser chemosensor with rapid responsivity and inherent memory based on a polymer of intrinsic microporosity," Sensors, vol. 11, no. 3, pp. 2478–2487.
- Weber J., Antonietti Q. Su, M., and Thomas A., 2007, "Exploring polymers of intrinsic microporosity -Microporous, soluble polyamide and polyimide," Macromolecular Rapid Communications, vol. 28, no. 18-19, pp. 1871–1876.
- 122. Yampol'skii Y. P., Pinnau I., and Freeman B. D., 2006, Materials Science of Membranes For Gas and Vapor Separation, John Wiley & Sons, Chichester, UK.
- 123. Yong W. F., Li F. Y., Xiao Y. C. et al., 2012, "Molecular engineering of PIM-1/Matrimidblend membranes for gas separation," Journal of Membrane Science, vol. 407-408, pp. 47–57.
- 124. Yingge Wang, Bader S. Ghanem, Zain Ali, Khalid Hazazi, Yu Han,\* and Ingo Pinnau, 2021, \*Recent Progress on Polymers of Intrinsic Microporosity and Thermally Modified Analogue Materials for Membrane-Based Fluid Separations , Small Struct., 2, 2100049 (p-1 of 29) © 2021 Wiley-VCH GmbH
- 125. Zhang L., Fang W., and Jiang J., 2011, "Effects of residual solvent
- 126. Ye, H., Zhang, C., Huo, C., Zhao, B., Zhou, Y., Wu, Y. & Shi, S. 2020. Advances in the Application of Polymers of Intrinsic Microporosity in Liquid Separation and Purification: Membrane Separation and Adsorption Separation. *Polymer Reviews*, 1-41.
- 127. Yin, H., Yang, B., Chua,, Y. Z., Szymoniak, P., Carta, M., Malpass-Evans, R., Mckeown, N. B., Harrison, W. J., Budd, P. M. & Schick, C. 2019. Effect of Backbone Rigidity on the Glass Transition of Polymers of Intrinsic Microporosity Probed by Fast Scanning Calorimetry. ACS Macro Letters, 8, 1022-1028.

- 128. Zhang, C., LI, P. & Cao, B. 2016a. Electrospun polymer of intrinsic microporosity fibers and their use in the adsorption of contaminants from a nonaqueous system. *Journal of Applied Polymer Science*, 133.
- 129. Zhang, C., LI, P., Huang, W. & Cao, B. 2016b. Selective adsorption and separation of organic dyes in aqueous solutions by hydrolyzed PIM-1 microfibers. *Chemical Engineering Research and Design*, 109, 76-85.
- 130. Zhang, J., JIN, J., Cooney, R. & Zhang, S. 2015. Fluoride-mediated polycondensation for the synthesis of polymers of intrinsic microporosity. *Polymer*, 76, 168-172.
- 131. Zhang, J., XU, W., Su, P., Xu, Z., Fan, Z. & Zhang, G. 2018. The Researches on Polymers of Intrinsic Microporosity Membranes for Separation. *E&ES*, 170, 052041.