

Final Technical Report
DE-SC0018181
PI: Jason E. Bara, co-PI: C. Heath Turner
The University of Alabama

Our DOE BES research grant (DE-SC0018181, 8/15/17-2/28/22) focused on the synthesis, characterization, and performance of a new class of polymers known as high-performance (HP)-ionenes as gas separation membranes, including associated computational studies. This research resulted in **11** peer-reviewed journal publications¹⁻¹¹ with an additional ~7 manuscripts currently in review or under preparation for submission. This DOE BES funding has also resulted in **3** U.S. patent applications.

Support from BES has enabled us to study gas separation mechanisms in membranes formed from HP-ionene materials with unprecedented structures. Polyimide-ionenes (and other forms of HP-ionenes also developed under this project) are unique in that they combine the desirable properties of aromatic polyimides (and other HP polymers) associated with state-of-the-art polymer membranes with imidazolium ILs. Our success with HP-ionene membranes is the result of logical retrosynthetic planning, molecular design, and a deep analysis of the requisite chemistries that result in tailored polymers that feature precisely spaced imide and imidazolium functional groups. This design strategy is augmented and guided by computational studies applied to understanding each aspect of the polyimide-ionene, from monomer structure to gas diffusion mechanisms through the membranes. New methodological computational approaches have emerged from this work, allowing us to connect the fundamental electrostatic interactions of individual monomers up to the larger-scale bulk polymer electrostatic environments. Furthermore, we have developed a kinetic Monte Carlo (KMC) strategy for translating the molecular-level information up to experimentally-relevant membrane performance data. The precise synthetic strategy used to create the tailored HP-ionene materials provided an exceptional opportunity to make fundamental connections between the polymer chemistry/structure and gas separation performance.

Research in DE-SC0018181 demonstrated that HP-ionenes can be processed into thin films through solvent and/or melt casting techniques and produce viable gas separation membranes. During the membrane fabrication process, stoichiometric amounts of ionic liquids (ILs) can also be added as a means of controlling polymer morphology, membrane properties, and gas permeability/selectivity. These “free” ILs are stabilized within the HP-ionene matrix and are not squeezed from the membrane under applied pressure, a behavior which had previously only been demonstrated for polyelectrolytes and simple ionenes.¹²

In this project, several HP-ionenes and composites with added ILs were observed to have modest gas permeabilities but excellent selectivity, especially for CO₂/CH₄ separation. Generally, the addition of “free” IL results in enhanced separation selectivity as well as increased gas permeability. Gas permeability in polyimide-ionenes and related materials appears to be governed by the enhanced organization/self-assembly arising from stronger associations between the rigid polymer chains caused by coulombic attractions, as compared to membranes comprised of poly(ILs) + ILs which are essentially a molecular-level “soup”. However, we discovered that the inclusion of the spirobisindane (SBI) moiety (commonly associated with polymer of intrinsic microporosity (PIMs)) within the polyimide-ionene backbone results in much higher gas permeabilities in polyimide-ionenes without sacrifice of CO₂ selectivity. This has led us to consider even more focused design strategies for enhancing separation. This includes rationally-planned molecular design strategies for synthesizing polyimide-ionene materials which contain high free volume elements such as SBI and ethanoanthracene (EA) (i.e., components of PIMs), and Tröger’s Base (TB) groups that are appropriately positioned within the polymer backbone and properly balanced by charged groups within the polymer backbone, as well as with added free IL. Furthermore, the viability of

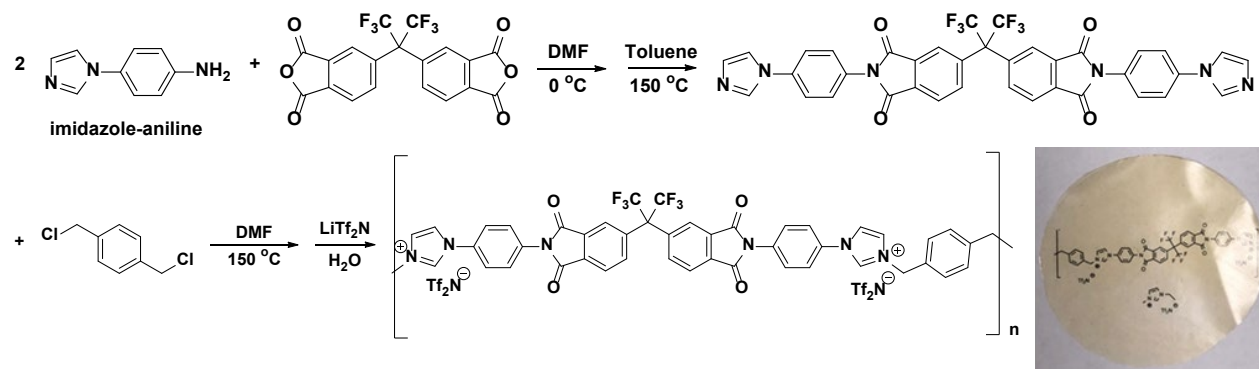
these synthetic strategies and the fundamental interactions resulting from these material designs can be uncovered via our corresponding simulation analyses.

All known ionenes are connected through two N atoms, such as the N(1) and N(3) positions of the imidazolium ring. In the context of gas separation membranes, there are no analogous neutral (i.e., uncharged) or partially charged polymers that can be synthesized by which to discern the true impact of the charged backbone on membrane performance. Recently, we have developed several new complementary synthetic methodologies which allow for polymer connectivity through the N(1) and C(2) atoms of the imidazole ring. We are the first to discover this approach and believe it is a powerful new design strategy by which to develop a systematic understanding of the effects of each individual component of the polymer on membrane performance, thus elucidating which component(s) have the greatest impact/influence on governing gas transport. This approach allows for the effect of charge to be understood by using polymers which possess the same backbone and differ only in the amount of charged moieties present within the backbone. Furthermore, this methodical design approach provides a direct bridge to the computational modeling studies, enabling a comprehensive molecular understanding of the emergent behavior.

Prior to our recent efforts, the vast majority of ionenes in the literature were relatively simplistic in structure, comprising ammonium cations tethered by long alkyl chains. Examples of ionenes as gas separation membranes were sparse, such as the relatively simple imidazolium ionene studied by Carlisle, Bara, and co-workers.¹² With support from DOE BES, we have demonstrated that ionenes with far more robust structures containing high free volume elements can be rationally designed and used as gas separation membranes. The crux of our approach has been a bottom-up design where monomer selection translates to polymers with desired qualities and membrane performances. Our studies of HP-ionenes with systematically varied structures enabled us to quantify the impact of molecular features on gas transport, both experimentally and computationally. To achieve these structures, we have relied on the use of versatile "imidazole-aniline" species, which we have economically prepared at scales up to 200 g with excellent yield. These imidazole-aniline molecules are key to the synthesis of polyimide-ionenes and TB-containing ionenes, and as will be shown later, they are the enabling components of the new PIM-TB ionenes we will study. The imidazole-aniline functionality is powerful in that it can be designed to impart control over the regiochemistry of the polymer backbone connectivity as well as the co-planarity of the adjacent imidazolium and benzene rings, both of which influence the local conformations of the polymer chain and the nature of the free volume regions of the membrane. It should also be noted that although ionenes have complex structures, PI Bara's group has routinely synthesized ionenes at scales of 100 g or more, and the new materials proposed in this work will be less expensive to synthesize than many other new types of gas separation membranes.

Scheme 1 depicts a general approach to the synthesis of imidazole-diimide monomers from the imidazole-aniline and a dianhydride (e.g., 6FDA). This monomer can then be reacted with suitable dihalide to produce a polyimide-ionene. Commercial dihalides (e.g., *p*-dichloroethylene) provide convenient co-monomers, while newly synthesized species such as dihalide-diamides can provide enhanced mechanical properties through H-bonding interactions.⁹

Scheme 1: Example synthesis of imidazole-diimide monomers and polyimide-ionene developed in our DE-SC0018181, along with picture of membrane formed from this material.



Scheme 1 represents just one of the many types of possible polyimide-ionenes that can be synthesized using our methods. To date, we have achieved high MW ($M_N > 75$ kDa) for all polyimide ionenes and nearly all of these materials are capable of forming thin films suitable for gas separation membranes. Polyimide-ionene materials with Tf₂N⁻ counter-anions generally exhibit thermal stabilities up to 400 °C and are soluble in polar organic solvents, including acetone, CH₃CN, DMF, DMSO and DMAc. We have also recently published our work on benzoxazole-containing ionene membranes with similar characteristics.¹⁰

The permeability of the example 6FDA polyimide-ionene in Scheme 1 was modest, with only ~2 barrer for CO₂. However, the inclusion of ILs within the 6FDA polyimide-ionene matrix generally increased permeability by 2-3×, with CO₂/N₂ and CO₂/CH₄ selectivity of 20-30 for both gas pairs. The amount and structure of IL added was observed to influence the polyimide-ionene morphology, which correlated with the changes in permeability and selectivity. The coordination between the polyimide-ionene and the ILs was stronger with the inclusion of 2 eq. of IL, with lower *d*-spacing values indicating that the chains are drawn closer around these ionic groups. The main halo was notably broadened (somewhat bimodal) by the incorporation of 2 eq. of IL, and the glass transition temperatures (T_g) of the IL-containing composites were reduced compared to the neat polyimide-ionenes. Thus, the nature and amount of IL added to polyimide-ionenes is clearly shown to influence polymer morphology and in turn, gas permeability.

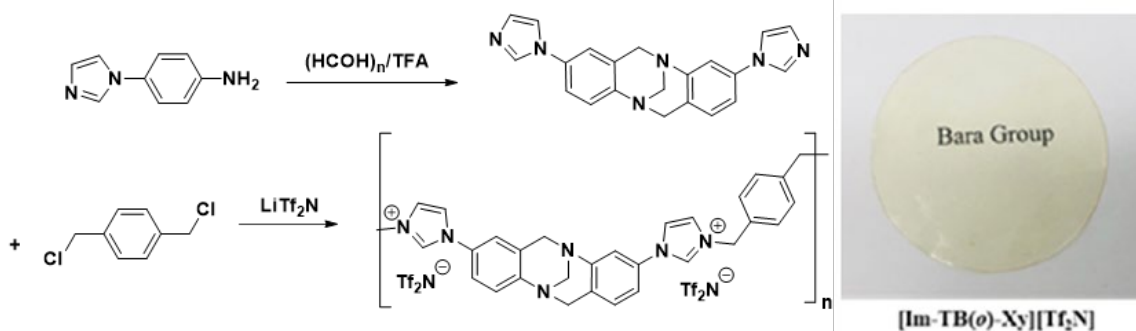
The effects of mixed anions (i.e., where the IL anion is not the same as that associated with the polyimide-ionene) on gas permeability and selectivity have also been of interest. However, smaller anions (e.g., BF₄⁻, PF₆⁻) tend to result in a more brittle polymer; producing quality membranes with anions other than Tf₂N⁻ has been challenging. While imidazolium cations with different functional groups (e.g., ethers, fluorinated groups) may also help us further understand how the IL cation structure influences membrane performance, we have found that modifications to the backbone are more influential to gas transport.

As our design of ionenes evolves toward structures that comprise the elements of PIMs, we have shown that our imidazole-aniline molecules are also ideal starting materials for the formation of TB-containing ionenes. The use of TB moieties in polymer backbones is a relatively recent development in gas separation membranes, and the TB group has been shown to impart excellent gas permeability and separation selectivity.¹³⁻²⁵ Scheme 2 depicts an example of a TB-containing ionene membranes which we studied in DE-SC0018181.³

The TB-containing ionenes synthesized this project are the first examples of materials wherein TB groups are directly connected to ions within a polymer backbone. Such combinations present exciting new directions for the rational design of polymer membranes that will allow for the elucidation of the neutral and ionic components' influence on gas transport mechanisms. Our TB-containing ionenes exhibit thermal stability up to ~400 °C (as measured by TGA, 5 °C/min, N₂) and can be formed into thin films suitable for use as membranes through solvent casting methods. These TB-containing ionenes

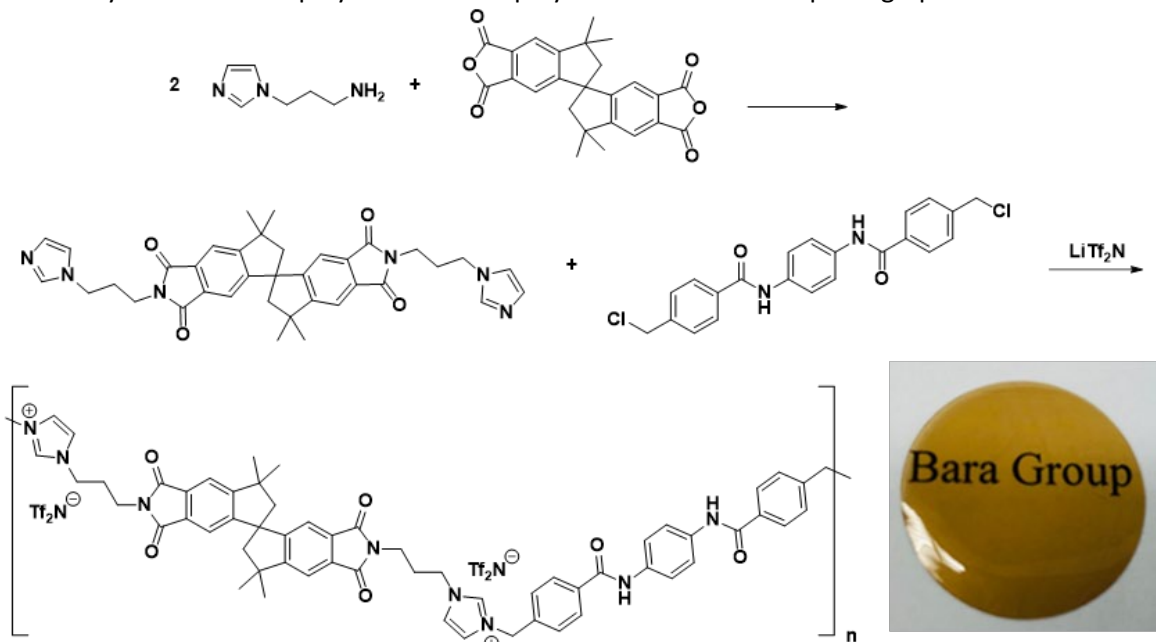
demonstrated modest CO₂ permeabilities in the range of 2 – 4 barrer but excellent CO₂/CH₄ selectivities up to 82.5. By comparing these TB-containing ionenes to other poly(IL), ionene and TB-containing materials (vis-à-vis Robeson Plots), we found that TB-containing ionenes were the most selective class of TB-containing polymer materials for CO₂/CH₄ separation.³ Thus, there is clearly synergy between the TB and ionic groups for this separation, and polymers containing both TB and ionic components warrant further investigation.

Scheme 2: TB-containing ionene polymer membrane from imidazole-aniline.



In our most ambitious approach to bottom-up membrane design, we have successfully realized the first combination of PIMs and ionenes through a multi-step synthesis using an SBI-containing dianhydride molecule originally reported by McKeown and co-workers.²⁶ The synthesis and structure of one example PIM-polyimide-ionene material is shown in Scheme 3.

Scheme 3: Synthesis of PIM-polyimide-ionene polymer membrane and photograph of membrane.



This PIM-polyimide-ionene membrane exhibits CO₂ permeability of ~300 barrer which is markedly higher than the other polyimide-ionenes and TB-containing ionenes, and CO₂/N₂ selectivity of 41, indicating that the SBI group is responsible for higher FFV than other diimide linkages (e.g. 6FDA) that we have used in ionenes. The PIM-polyimide-ionene is also soluble in a range of organic solvents and was

thermally stable up to 400 °C (as measured by TGA, 5 °C/min, N₂).¹¹ These results are encouraging as they suggest that the presence of SBI and EA groups may be a key factor to increasing permeability in ionenes, without sacrificing selectivity. Furthermore, the presence of ionic components may stabilize PIMs and slow/stop aging via non-covalent crosslinks which stabilize polymer microstructure as the IL can migrate within and between ionic domains of polymer chains.

The fundamental knowledge gained in DE-SC0018181 illustrates that ionenes and ionene + IL composites are a viable and versatile class of materials for the rational design of gas separation membranes with tailored properties that can provide performances to meet the demands required to achieve cost and energy efficient chemical separations in the 21st Century.

Our successes in DE-SC0018181 with ionenes as gas separation membranes with rationally designed structures has given us a set of guidelines as to how both the ionene structure and added IL influence gas transport and separation selectivity. Will we be able to implement those lessons learned to develop novel and transformative polymer membrane materials systematically probe and understand the synergistic effects of PIM-TB and ionic components. In future work, we will build upon polymer backbones that are much more intrinsically permeable, and we will examine the effects of ionic groups and ILs on materials which already perform at or above Robeson's Upper Bounds, such that the impacts of our studies are highly pertinent to the forefront of the gas separation membrane field. We will also leverage the large and growing body of knowledge associated with TB and PIM-containing materials to create membranes that move closer to gas phase mass transfer limited separations.

REFERENCES

1. Szala-Bilnik J, Crabtree E, Abedini A, Bara JE, Turner CH. Solubility and diffusivity of CO₂ in ionic polyimides with [C(CN)₃]_x[oAc]_{1-x} anion composition. *Computational Materials Science*. 2020;174:109468. doi: <https://doi.org/10.1016/j.commatsci.2019.109468>.
2. Abedini A, Crabtree E, Bara JE, Turner CH. Molecular analysis of selective gas adsorption within composites of ionic polyimides and ionic liquids as gas separation membranes. *Chem Phys*. 2019;516:71-83. doi: 10.1016/j.chemphys.2018.08.039.
3. Kammakam I, O'Harra KE, Bara JE, Jackson EM. Design and Synthesis of Imidazolium-Mediated Tröger's Base-Containing Ionene Polymers for Advanced CO₂ Separation Membranes. *ACS Omega*. 2019;4(2):3439-48. doi: 10.1021/acsomega.8b03700.
4. Bara JE, O'Harra KE. Recent Advances in the Design of Ionenes: Toward Convergence with High-Performance Polymers. *Macromolecular Chemistry and Physics*. 2019;220(13):1900078. doi: 10.1002/macp.201900078.
5. Bara JE, Finotello A, Magee JW, Qian S, O'Harra KE, Dennis GP, Noble RD. 110th Anniversary: Properties of Imidazolium-Based Ionic Liquids Bearing Both Benzylic and n-Alkyl Substituents. *Industrial & Engineering Chemistry Research*. 2019;58(38):17956-64. doi: 10.1021/acs.iecr.9b03159.
6. Szala-Bilnik J, Abedini A, Crabtree E, Bara JE, Turner CH. Molecular Transport Behavior of CO₂ in Ionic Polyimides and Ionic Liquid Composite Membrane Materials. *The Journal of Physical Chemistry B*. 2019;123(34):7455-63. doi: 10.1021/acs.jpcc.9b05555.
7. O'Harra KE, Kammakam I, Bara JE, Jackson EM. Understanding the effects of backbone chemistry and anion type on the structure and thermal behaviors of imidazolium polyimide-ionenes. *Polymer International*. 2019;68(9):1547-56.
8. O'Harra KE, Kammakam I, Devriese EM, Noll DM, Bara JE, Jackson EM. Synthesis and Performance of 6FDA-Based Polyimide-Ionenes and Composites with Ionic Liquids as Gas Separation Membranes. *Membranes*. 2019;9(7):79.

9. Kammakakam I, Bara JE, Jackson EM. Synthesis and characterization of imidazolium-mediated Tröger's base containing poly(amide)-ionenes and composites with ionic liquids for CO₂ separation membranes. *Polymer Chemistry*. 2020;11(46):7370-81. doi: 10.1039/D0PY01038C.
10. Kammakakam I, O'Harra KE, Jackson EM, Bara JE. Synthesis of imidazolium-mediated Poly(benzoxazole) Ionene and composites with ionic liquids as advanced gas separation membranes. *Polymer*. 2020:123239. doi: <https://doi.org/10.1016/j.polymer.2020.123239>.
11. Kammakakam I, O'Harra KE, Bara JE, Jackson EM. Spirobisindane-Containing Imidazolium Polyimide Ionene: Structural Design and Gas Separation Performance of "Ionic PIMs". *Macromolecules*. 2022;55(11):4790-802. doi: 10.1021/acs.macromol.1c02317.
12. Carlisle TK, Bara JE, Lafrate AL, Gin DL, Noble RD. Main-chain imidazolium polymer membranes for CO₂ separations: An initial study of a new ionic liquid-inspired platform. *J Membr Sci*. 2010;359(1-2):37-43. doi: 10.1016/j.memsci.2009.10.022. PubMed PMID: ISI:000279953300005.
13. Sanaeepur H, Ebadi Amooghin A, Bandehali S, Moghadassi A, Matsuura T, Van der Bruggen B. Polyimides in membrane gas separation: Monomer's molecular design and structural engineering. *Prog Polym Sci*. 2019;91:80-125. doi: 10.1016/j.progpolymsci.2019.02.001.
14. Zhang C, Fu L, Tian Z, Cao B, Li P. Post-crosslinking of triptycene-based Troger's base polymers with enhanced natural gas separation performance. *J Membr Sci*. 2018;556:277-84. doi: 10.1016/j.memsci.2018.04.013.
15. Ma X, Abdulhamid MA, Pinnau I. Design and Synthesis of Polyimides Based on Carbocyclic Pseudo-Troger's Base-Derived Dianhydrides for Membrane Gas Separation Applications. *Macromolecules (Washington, DC, U S)*. 2017;50(15):5850-7. doi: 10.1021/acs.macromol.7b01054.
16. Ma X, Abdulhamid M, Miao X, Pinnau I. Facile Synthesis of a Hydroxyl-Functionalized Tröger's Base Diamine: A New Building Block for High-Performance Polyimide Gas Separation Membranes. *Macromolecules (Washington, DC, U S)*. 2017;50(24):9569-76. doi: 10.1021/acs.macromol.7b02301.
17. Zhuang Y, Seong JG, Do YS, Lee WH, Lee MJ, Cui Z, Lozano AE, Guiver MD, Lee YM. Soluble, microporous, Troger's Base copolyimides with tunable membrane performance for gas separation. *Chem Commun (Cambridge, U K)*. 2016;52(19):3817-20. doi: 10.1039/C5CC09783E.
18. Zhuang Y, Seong JG, Do YS, Lee WH, Lee MJ, Guiver MD, Lee YM. High-strength, soluble polyimide membranes incorporating Troger's Base for gas separation. *J Membr Sci*. 2016;504:55-65. doi: 10.1016/j.memsci.2015.12.057.
19. Seong JG, Zhuang Y, Kim S, Do YS, Lee WH, Guiver MD, Lee YM. Effect of methanol treatment on gas sorption and transport behavior of intrinsically microporous polyimide membranes incorporating Troger's base. *J Membr Sci*. 2015;480:104-14. doi: 10.1016/j.memsci.2015.01.022.
20. Carta M, Croad M, Malpass-Evans R, Jansen JC, Bernardo P, Clarizia G, Friess K, Lanc M, McKeown NB. Triptycene Induced Enhancement of Membrane Gas Selectivity for Microporous Troeger's Base Polymers. *Adv Mater (Weinheim, Ger)*. 2014;26(21):3526-31. doi: 10.1002/adma.201305783.
21. Tocci E, De Lorenzo L, Bernardo P, Clarizia G, Bazzarelli F, McKeown NB, Carta M, Malpass-Evans R, Friess K, Pilnacek K, Lanc M, Yampolskii YP, Strarannikova L, Shantarovich V, Mauri M, Jansen JC. Molecular Modeling and Gas Permeation Properties of a Polymer of Intrinsic Microporosity Composed of Ethanoanthracene and Troger's Base Units. *Macromolecules (Washington, DC, U S)*. 2014;47(22):7900-16. doi: 10.1021/ma501469m.
22. Wang Z, Wang D, Jin J. Microporous Polyimides with Rationally Designed Chain Structure Achieving High Performance for Gas Separation. *Macromolecules (Washington, DC, U S)*. 2014;47(21):7477-83. doi: 10.1021/ma5017506.
23. Wang Z, Wang D, Zhang F, Jin J. Troger's Base-Based Microporous Polyimide Membranes for High-Performance Gas Separation. *ACS Macro Lett*. 2014;3(7):597-601. doi: 10.1021/mz500184z.

24. Zhuang Y, Seong JG, Do YS, Jo HJ, Cui Z, Lee J, Lee YM, Guiver MD. Intrinsically Microporous Soluble Polyimides Incorporating Troger's Base for Membrane Gas Separation. *Macromolecules* (Washington, DC, U S). 2014;47(10):3254-62. doi: 10.1021/ma5007073.
25. Carta M, Malpass-Evans R, Croad M, Rogan Y, Jansen JC, Bernardo P, Bazzarelli F, McKeown NB. An Efficient Polymer Molecular Sieve for Membrane Gas Separations. *Science*. 2013;339(6117):303. doi: 10.1126/science.1228032.
26. Rogan Y, Starannikova L, Ryzhikh V, Yampolskii Y, Bernardo P, Bazzarelli F, Jansen JC, McKeown NB. Synthesis and gas permeation properties of novel spirobisindane-based polyimides of intrinsic microporosity. *Polymer Chemistry*. 2013;4(13):3813-20. doi: 10.1039/C3PY00451A.