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Increasing M₂(dobdc) Loading in Selective Mixed-Matrix Membranes: A Rubber Toughening Approach

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Supporting Information

ABSTRACT: Mixed-matrix membranes (MMMs) were formed by incorporating $M_2(dobdc)$ (M = Mg, Ni; dobdc⁴⁻ = 2,5-dioxido-1,4-benzenedicarboxylate) metal-organic framework (MOF) nanoparticles in a series of poly(ether-imide) copolymers. Addition of the MOF nanoparticles improved the permeability of H₂, N₂, CH₄, and CO₂ relative to the pure copolymer by increasing gas solubility and, in most cases, diffusivity. More limited improvements in diffusivity were observed for the more strongly adsorbing gases. Because of such transport considerations, improvements in permeability and selectivity were most pronounced for H_2/CH_4 and H_2/N_2



separations. Incorporation of a greater ether content within the copolymers led to the formation of defect-free MMMs by physically sealing polymer-MOF interfacial defects, allowing higher MOF loadings to be achieved. For Mg₂(dobdc), selective, defect-free films could be formed with loadings of up to 51 wt %. However, at these high loadings, films became weak and brittle. The mechanical properties of the composite materials were therefore quantified by tensile tests and compared to those of the neat polymers used commercially for membrane film formation. High contents of flexible ether units and small MOF nanoparticle sizes were found to be necessary to form strong and ductile MMMs, although clear trade-offs exist between transport performance, MOF loading, and mechanical properties. These trade-offs are critically examined to evaluate the current limitations and potential benefits to forming M_2 (dobdc) MMMs using this rubber toughening approach.

1. INTRODUCTION

Today, commercial gas separation membranes used in industry are polymeric.¹ Unlike inorganic materials, many polymers are solution processable and, therefore, can be formed into continuous films with the requisite strength and ductility needed for deployment in industry. The relative ease of fabricating thin polymer films has enabled the use of membranes for a variety of hydrogen separations, including syngas ratio adjustment and ammonia purge gas recovery, nitrogen generation for on-board inert gas generation systems, and in competition with amine absorption, natural gas sweetening.² It is envisioned that new polymeric materials could help improve performance for current and emerging applications, thereby extending the acceptance and application of membrane-based separations in industry.

While current polymers have proven applicability, all commercial gas separation membranes achieve separation efficiency via the solution-diffusion mechanism,³ and the best combinations of permeability and selectivity that can be achieved by this mode of transport are limited by the so-called Robeson Upper Bound.⁴ On the other hand, transport properties in permanently porous materials, such as zeolites, carbons, and metal-organic frameworks (MOFs), are not bounded by the Robeson limit. Unlike polymers, these materials are very difficult to process. If practical methods could be identified for processing porous materials into mechanically robust, high surface area thin films, these materials

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Figure 1. Synthesis of poly(ether-imide) copolymers.

could significantly improve efficiency and productivity for current membrane-based gas separations. 1

To balance the need for improved transport performance with the processability of polymers, one particularly attractive approach is dispersing porous materials within polymers to form hybrid materials known as mixed-matrix membranes (MMMs).^{5,6} In general, the porous component of MMMs improves separation performance through a size-sieving mechanism. At the laboratory scale, carbon-molecular sieves and zeolites have been particularly successful in demonstrating the benefit to this approach,^{7–9} and more recently, zeolitic imidazolate frameworks (ZIFs) have shown extraordinary size-based sieving properties for separating propylene from propane.^{10–13}

Recently, MOFs of the type $M_2(dobdc)$, also known as M-MOF-74, or CPO-74-M, where M = Mg, Mn, Fe, Co, Ni, Cu, or Zn and dobdc⁴⁻ = 2,5-dioxido-1,4-benzenedicarboxylate, have shown promising adsorption-based separation performance for CO₂ and olefin/paraffin separations.^{14–16} Moreover, when formed into nanoparticles and dispersed in polyimides, these MOFs can significantly improve membrane-based separations.^{17–19} For gas mixtures, the competitive nature of the binding sites in $M_2(dobdc)$ can further improve performance,¹⁸ and from the standpoint of chemical stability, nanoparticles formed from these MOFs can interact with certain polymer functionalities, such as those found in polyimides, inducing some degree of physical or chemical cross-linking and thereby reducing the susceptibility of the MMMs to plasticization.^{18,19}

Nevertheless, there are still many questions concerning the real-world applicability of M_2 (dobdc) MMMs, and, more broadly, the applicability MMMs as a viable platform in general.

Of particular importance is the effect of the included inorganic particles on the mechanical properties of the membranes, and relatedly, the trade-off between particle loading and processability for these films. Unfortunately, despite the abundance of transport data on MMMs available in the literature, very few reports are available on the mechanical properties of these systems.

Some of the most extensive data on mechanical properties for MOF-based MMMs surrounds ZIF-8. Early research in this area reported embrittlement and a reduction in film strength for increased particle loading in ZIF-8/Matrimid MMMs.²⁰ Embrittlement was apparent at loadings of 30 wt %, and decreases in selectivity were observed for very high loadings of 60 wt %.²⁰ More in-depth studies investigating ZIF-8 MMM mechanical properties, including tensile, dynamic mechanical analysis (DMA), and nanoindentation studies have recently been reported.^{21,22} These results suggest extraordinary differences can be achieved in mechanical properties for composites made from glassy polymers, such as Matrimid, which has a glass transition temperature (T_g) of approximately 345 °C, and rubbery polymers, such as polyurethane, which has a T_{σ} of -32°C. For Matrimid-based MMMs, detrimental mechanical properties have been observed for loadings between approximately 10-15 wt %, while ductile films formed from polyurethane-based MMMs could be formed with ZIF-8 loadings of up to 40 wt %.^{21,22} Very recently, some quantitative mechanical properties have been reported for MMMs formed from UiO-66-based MOFs, PAF-1, and fumed silica in several glassy polymer matrixes.²³ These results are consistent with the data presented here. Films become weaker and more brittle with increased nanocomposite loading. Interestingly, the authors note that in certain cases mechanical properties can improve with time for MMMs, indicating a reversal to the typical embrittlement induced by physical aging in neat glassy polymers.^{23,24}

Herein, we seek to investigate the trade-off between polymer rigidity, MOF loading, and MOF compatibility for the emerging area of MMMs formed with M_2 (dobdc) nanocrystals. To this end, a series of poly(ether-imide) copolymers have been synthesized. The imide segment is a high-performance polyimide known as 6FDA-durene, which is formed from 4,4'-(hexafluoroisopropylidene) diphthalic anhydride, 6FDA, and 2,3,5,6-tetramethyl-1,4-phenylenediamine, durene.²⁵ The ether segment is formed from a polyether diamine and 6FDA. By combining the properties of a rigid 6FDA-durene polymer, which has one of the highest detectible T_g 's of a polyimide, with a low- T_g polyether, a rubber toughening-type approach is investigated for a variety of copolymers with diverse physical and morphological characteristics.²⁶ These copolymers have been combined with recently developed MOF nanoparticles, Mg₂(dobdc) and Ni₂(dobdc), and correlations between MOF loading, film strength and ductility, and transport properties are presented. Our findings indicate that a higher MOF loading can be achieved in the more flexible films. However, for the gases considered, increasing soft block content resulted in a significant divergence of permeability and selectivity property sets away from the Robeson Upper Bound front, thereby outweighing the relative improvements in transport properties that were gained by increasing MOF loading.

2. EXPERIMENTAL SECTION

2.1. Synthesis of Copolymers. Copolymers were synthesized from a dianhydride and diamines using standard chemical imidization techniques.27' The dianhydride used for these experiments, 2,2'bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA), was purchased from TCI (H0771), and two diamines, 2,3,5,6-tetramethyl-1,4-phenylenediamine (durene) and O,O'-bis(2-aminopropyl) polypropylene glycol-block-polyethylene glycol-block-polypropylene glycol (Jeffamine ED-2003), were purchased from TCI (T1457) and Sigma-Aldrich (14529), respectively. Durene was purified twice by recrystallization from methanol and 6FDA was purified by vacuum sublimation. Monomers were stored in a vacuum oven at 60 °C prior to use. Jeffamine ED-2003 was used as received. N-Methyl-2pyrrolidone (NMP) and triethylamine (Et₃N) were purchased from Spectrum (M1557) and EMD (TX1200-5), respectively, and were vacuum-distilled prior to use. Acetic anhydride was purchased from Sigma-Aldrich (320102) and used as received. All synthesis glassware and Teflon adaptors were dried at 125 °C for 24 h prior to use.

A three-neck round-bottom flask equipped with a nitrogen purge and an overhead mechanical stirrer was used for the syntheses. House nitrogen flowed through a Drierite column (Sigma-Aldrich, Z112879) before entering the three-neck flask. After establishing nitrogen flow in the three-neck flask, the glassware was flame-dried with a methane torch to desorb water vapor adsorbed on the interior walls of the glassware.

Four polymers were synthesized for this project, including a polyimide, 6FDA-durene, which will be hereafter referred to as J0, and three copolymers, containing various amounts of copolymerized imide and polyether segments. A schematic for the synthesis of these copolymers is presented in Figure 1. The three poly(ether-imide) compositions synthesized contained 1, 5, and 10 mol % Jeffamine ED-2003 per total moles of monomer. Hereafter, these samples will be referred to as J1, J5, and J10, where J1, for example, refers to a copolymer of 6FDA-durene:Jeffamine that contains 1 mol % of Jeffamine ED-2003, 49 mol % durene diamine, and 50 mol % 6FDA.

Formation of the polyimide, J0, was carried out as follows. To the flame-dried three-neck flask, 3.44 g (21.0 mmol) of durene diamine was dissolved in 23.3 mL of NMP. After dissolution, an ice bath was

added under the reaction flask, followed by the slow addition of 9.31 g (21.0 mmol) of 6FDA and 23.3 mL of NMP. The monomers were allowed to react under N2 flow for approximately 24 h to form a viscous poly(amic acid) solution. The polyimide was cyclized through chemical imidization by adding 2.9 mL (21 mmol) of Et₃N and 7.9 mL (84 mmol) of acetic anhydride. An additional 9.0 mL of NMP was added to the reaction flask, and the reaction proceeded for 24 h. The highly viscous solution was then diluted with an additional 78.9 mL of NMP and precipitated in a 1 L container of methanol, which was left stirring on a stir plate. To extract the synthesis solvent, the white polymer fibers were washed with 1 L of fresh methanol, vacuumfiltered dry, and stirred in fresh methanol for 24 h followed by a second washing, filtration, and stirring step for an additional 24 h. The fibers were then dried at 230 °C for 16 h under vacuum to remove any residual solvent. Solvent removal was confirmed by thermogravimetric analysis (TGA).

Synthesis of the copolymers was performed similarly to that of the pure polyimide, J0. However, instead of adding equimolar amounts of 6FDA and durene to the reaction vessel, varying compositions of durene and Jeffamine ED-2003 diamines were added simultaneously. One-to-one molar compositions between the dianhydride and diamine were always strictly maintained. For the copolymers, 6FDA-durene segments will be referred to as the hard block and 6FDA-Jeffamine ED-2003 poly(ether-imide) segments will be referred to as the soft block.

The syntheses of copolymers were carried out as follows. For J1, monomer compositions were 2.99 g (18.2 mmol) of durene, 0.750 g (0.372 mmol) of Jeffamine ED-2003, and 8.26 g (18.6 mmol) of 6FDA; for J5, monomer compositions were 2.24 g (13.6 mmol) of durene, 3.03 g of Jeffamine ED-2003 (1.52 mmol), and 6.73 g of 6FDA (15.2 mmol); for J10, monomer compositions were 1.62 g (9.84 mmol) of durene, 4.93 g (2.46 mmol) of Jeffamine ED-2003, and 5.46 g (12.3 mmol) of 6FDA. For all reactions, 1 mol of Et₃N and 4 mol of acetic anhydride were used per mole of the final polymer repeat unit.

2.2. Synthesis of MOF Nanocrystals. Nanocrystals were synthesized at room temperature using a rapid nucleation technique similar to that described previously.¹⁷ Solid $Mg(NO_3)_2 \cdot 6H_2O$ (4.20 g, 16.4 mmol), purchased from Sigma-Aldrich (237175), and 2,5dihydroxyterephthalic acid (dobdc) (1.01 g, 5.10 mmol), purchased from TCI (D3899), were added to a 1 L round-bottom flask equipped with a magnetic stir bar. Next, dimethylformamide (DMF), ethanol, and water were added to the flask in a ratio of 405:27:27 mL, and the ligand and metal salt were stirred rapidly for approximately 30 min. Triethylamine was then added in 1 mL aliquots until a total of 8 mL had been added. Cloudiness in the reaction vessel was observed after adding approximately 5 mL, indicating the onset of nanoparticle formation. The solution was stirred rapidly for 2 h, although no color change was observed after the addition of Et₃N, suggesting that nanoparticle formation occurs over a much shorter time scale. After the reaction, the resulting solution was centrifuged and the supernatant solution was discarded. The nanoparticles were rinsed five times with 250 mL of DMF to remove unreacted ligand. These washing steps were performed by resuspending the nanoparticles in DMF, heating the solution at 120 °C for ~1 h, concentrating the nanoparticles by centrifugation, and pouring off the supernatant solution. Five rinses with 250 mL of methanol were performed to exchange DMF from the MOF. These exchanges consisted of resuspending the nanoparticles in methanol, heating to 60 °C for ~1 h, concentrating the nanoparticles by centrifugation, and pouring off the supernatant solution. Methanol exchange was confirmed by FT-IR spectroscopy, and the Mg₂(dobdc) nanocrystals were stored in a stock suspension of methanol until use. Nickel-containing nanoparticles were prepared in a similar fashion, with the only exception being that Ni(NO₃)₂·6H₂O (Sigma-Aldrich, 203874) was used for the synthesis instead of $Mg(NO_3)_2$ ·6H₂O. Details concerning the shape and size of these particles were reported in our previous work.¹⁸

2.3. Film Formation. Neat polymer films were formed by first dissolving the polymer powder in dichloromethane and then casting solutions into glass rings that were attached to flat glass plates by



Figure 2. (A) ¹H NMR spectra indicating addition of PEO-type segments into the polyimide backbone and (B) TGA profiles for copolymers collected at a ramp rate of 10 $^{\circ}$ C/min. Horizontal lines indicate expected mass loss from thermal degradation of the targeted polyether soft block composition.

silicone caulk. All polymer solutions were filtered with a 1 μ m syringe filter purchased from Whatman (889-33367).

To prepare MMMs with targeted nanoparticle loadings, the concentration of the nanoparticle stock solutions needed to be determined. To estimate the concentration, 1 mL of the well-dispersed, sonicated solution was slowly dried and activated at 180 $^\circ$ C, and the mass of dried nanoparticles was measured.

With the concentration of nanoparticle stock solutions determined, mixed-matrix films were prepared as follows. Aliquots of the nanoparticle solutions corresponding to a given mass of activated nanoparticles were pipetted from the stock solution and resuspended in dichloromethane. Methanol, the suspending liquid in the stock suspension, is a nonsolvent for the polymers, and needed to be removed to prevent phase separation when casting films. The dichloromethane-suspended nanoparticles were added to a filtered dichloromethane/polymer solution and directly sonicated at 50% amplitude for 30 s using a QSonica probe sonicator (model Q55). The mixed-matrix solutions containing Ni2(dobdc) were further filtered with a 1 μ m syringe filter. However, because of particle agglomeration, attempts to filter Mg₂(dobdc) casting solutions resulted in significant retention of the nanoparticles, which made it difficult to achieve high mass loadings, so these solutions were not filtered before casting. With use of the calculated concentration of MOF stock solution, films of approximately 30 wt % M2(dobdc) were cast. In addition, one film with approximately 50 wt % Mg₂(dobdc) was cast for the J10 polymer. Films were approximately 40–60 μ m thick.

2.4. Gas Transport Measurements. Pure-gas permeabilities were determined from a constant volume-variable pressure pure-gas permeator,²⁸ and samples were supported on brass shim stock disks similar to a procedure described previously.²⁹ All polymer films and mixed-matrix films were preactivated at 120 °C under dynamic vacuum for at least 2 h in a vacuum oven and then fully activated at 180 °C under dynamic vacuum for approximately 4 h in the permeation cell. After activation, permeation experiments were peformed in the following order: H₂, CH₄, N₂, and CO₂. For H₂, CH₄, and N₂, pressures up to 60 bar in 5 bar increments were measured, and for CO₂, pressures up to 50 bar were measured. All permeation tests were performed at 35 °C unless otherwise specified. Additionally, low pressures were considered for H2, N2, and CO2. For H2 and CO2, lowpressure data were collected at 0.1, 0.15, 0.25, 0.5, 0.75, and 1.0 bar, and for N₂, low-pressure data were collected at 0.25, 0.5, 0.75, and 1.0 bar. For CH₄, samples were also tested at 1 bar. To investigate the effect of conditioning and plasticization, CO2 hysteresis loops were investigated on the polymer and Mg₂(dobdc) mixed-matrix films. Each

data point was held for 6 times the time lag at the lowest pressure

probed, unless the time lag was too short to determine. In those cases, samples were held for 3 min at each pressure. The time lag is defined as the intercept of the steady-state permeation rate with the *x*-axis, which has classically been used to describe diffusion relationships in polymers that obey the solution-diffusion model.³⁰ The permeability, *P*, of gas *i* was calculated according to the following equation:

$$P_{i} = \frac{V_{\rm D}l}{p_{2}ART} \left[\left(\frac{\mathrm{d}p_{i}}{\mathrm{d}t} \right)_{\rm ss} - \left(\frac{\mathrm{d}p_{i}}{\mathrm{d}t} \right)_{\rm leak} \right]$$
(1)

where $V_{\rm D}$ is the calibrated downstream volume, l is the film thickness, A is the area of film accessible to gas transport, R is the ideal gas constant, T is the absolute temperature, and $\left(\frac{\mathrm{d} p_i}{\mathrm{d} t}\right)$ is the downstream pressure rise with respect to time at steady-state permeation (subscript "ss") and when the system is sealed (i.e., the leak rate, subscript "leak"). Ideal selectivities were calculated as the ratio of pure-gas permeabilities.

2.5. Characterization and Mechanical Testing. Proton nuclear magnetic resonance (¹H NMR) experiments were performed on a 400 MHz instrument with chloroform-*d* (Cambridge Isotope, DLM-7-100) as the solvent. Thermogravimetric analysis (TGA) was performed with a TA Instruments Q5000 instrument using UHP N₂ as the atmosphere for the balance and furnace gas and a heating rate of 10 °C/min. Glass transition temperatures were determined using a TA Instruments Q800 Dynamic Mechanical Analyzer (DMA). Samples were heated at 3 °C/min with an applied frequency of 1 Hz and a constant amplitude of 15 μ m unless otherwise specified. Powder X-ray diffraction experiments were performed on a Bruker D8 ADVANCE instrument.

Static mechanical testing was performed in room-temperature air using an Instron 5944 screw-driven Universal Testing Machine under displacement rate control at a displacement rate of 1.3 mm/s following the ASTM Standard D1708 mechanical testing protocol.³¹ At least four separate samples were tested for each experiment. Samples were prepared by cutting dumbbell-shaped films from larger films using an ASTM D1708 certified cutting die from Pioneer-Dietecs (Weymouth, MA). For the mixed-matrix films, considerable variability was observed in the elongation at break, so figures show data for samples with the highest elongation at break recorded.

For cross-sectional transmission electron microscopy (TEM), MMMs were imbedded in epoxy resin (Araldite 502, Electron Microscopy Sciences) and cured at 60 $^{\circ}$ C for 12 h. The samples were then cut into ~100 nm thick sections using an RMC MT-X Ultramicrotome (Boeckeler Instruments) and collected on copper TEM grids. TEM images were obtained on a JEOL 1200 EX TEM instrument operating at an accelerating voltage of 120 kV.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Formation of Polymer and Mixed-Matrix Films. Copolymers were prepared by synthesizing varying degrees of polyether soft block units into the imide backbone. ¹H NMR data, presented in Figure 2A, are particularly relevant for this structural analysis. Peaks with chemical shifts characteristic of 6FDA and durene at approximately 7.96-8.16 and 2.12-2.22 ppm, respectively, appear for each polymer, confirming the incorporation of imide functionality into the polymer backbone.³² Noticeable differences in the spectra result from incorporation of the polyether soft block, the most dramatic of which are peaks characteristic of poly(ethylene oxide) (PEO), which are found at 3.68 ppm. The intensity of the PEO peak increases concomitantly with the increasing content of the soft block and provides a useful comparative peak for determining the amount of soft block experimentally incorporated into the copolymer. By comparison of peak intensities of PEO to 6FDA and durene functionalities, the actual molar composition for each copolymer was found to closely match the targeted compositions. For example, the J10 sample, which had a targeted polyether content of 10 mol % had an experimentally determined polyether content of ~9 mol %. Similar results were observed for the other copolymers (Supporting Information S.1).

Each copolymer also exhibited excellent thermal stability, showing no degradation under N2 until temperatures above 300 °C (Figure 2B). MMMs formed with an inorganic phase containing open metal sites, such as the MOFs considered in this work, require thermal stability of the polymer phase beyond that of the activation temperature. Because $M_2(dobdc)$ nanocrystals require activation at 180 °C, the copolymers synthesized here are thermally compatible with these systems. Additionally, the two-stage mass loss in these thermal heating profiles is consistent with degradation of the soft block before degradation of the hard block, similar to partially pyrolized membranes formed by the degradation of PEO-containing side chains.³³ We observed mass losses consistent with total decomposition of the soft block between approximately 450 and 500 °C followed by decomposition of the hard block above 500 °C. Moreover, these results support our observations from ¹H NMR spectroscopy. The weight loss from soft block degradation, highlighted by dashed lines in Figure 2B, closely match the total targeted soft block content in each copolymer. The slight mass loss for J5 between 300 and 350 °C likely relates to some degree of low molecular weight oligomers in the polymer film. Copolymer J5 had the lowest relative molecular weight of samples synthesized for this study (Supporting Information S.2).

To examine the effects and potential limitations of this hard block/soft block approach, film loadings of ~30 wt % were targeted. Under these loadings, nonselective defects are often formed for MMMs based upon glassy polymers, which has resulted in significant efforts to understand the interactions between the rigid filler and polymer matrix.³⁴ Previous work demonstrated that incorporation of rubbery, siloxane functionality into a polyimide backbone to form a poly(imide-*co*siloxane) increased interfacial interactions with carbon nanotubes, thereby eliminating defects.³⁵ A similar strategy is investigated here; however, polymers have been synthesized with varying degrees of soft block content to elucidate the role of the soft block on sealing nonselective defects at the MOF– polymer interface. A list of samples considered in this study is presented in Table 1. For the copolymer containing the highest

Table 1. Mass Fraction of $Mg_2(dobdc)$ and $Ni_2(dobdc)$ in Mixed-Matrix Films

sample name	Ni ₂ (dobdc)	$Mg_2(dobdc)$
J0 (20)	20 wt %	
J0 (28)		28 wt %
J1 (28)		28 wt %
J5 (27)		27 wt %
J10 (21)	21 wt %	
J10 (39), J10 (51)		39, 51 wt %

content of soft block, J10, an additional film was formed with 51 wt % Mg₂(dobdc), which, to the best of our knowledge, is the highest content for M₂(dobdc) nanoparticles yet supported in a continuous film. However, at this high MOF loading, the film was qualitatively weak and brittle, precluding quantitative mechanical characterization by DMA and Instron experiments, as described later. Furthermore, two additional Ni₂(dobdc) containing MMMs were formed with J0 and J10.

Polyethers are often semicrystalline, a material property known to decrease permeability.³⁶ Moreover, Jeffamine ED-2003 in its pure form has a crystalline morphology with a crystalline melting temperature of ~40 °C.³⁷ To investigate the morphological nature of the samples prepared for this study, powder X-ray diffraction patterns are presented for the neat polymers in Figure 3A and for the MMMs in Figure 3B. No clear crystallinity for the pure polymers was detected within the resolution of these experiments. Additionally, DSC experiments further confirmed the absence of crystallinity for the J10 sample, which had the largest contribution of polyether content (Supporting Information S.3). Furthermore, powder diffraction analysis of MMMs reveals that the MOF nanoparticles maintain their crystalline structure after film formation.

Peak maxima from the amorphous halos of the diffraction patterns were used to calculate *d*-spacing using the Bragg equation. These results, presented in Table 2, indicate the most probable distance between neighboring polymer chains.³⁸ For the pure polymers, d-spacing decreases from 6.31 Å for J0 to 5.72 Å for J10. This decrease indicates a denser polymer structure for the polyether-containing copolymers, which, as will be discussed later, correlates with a decreasing trend in gas permeability. Addition of Mg₂(dobdc) nanoparticles also resulted in significant reductions in d-spacing from the amorphous halos of the polymer films, which suggests that the MOF nanoparticles have favorable interactions with the polyimide and copolymer functionality. A similar analysis was attempted with the Ni₂(dobdc) and J10 (51) films, but overlapping peaks between the crystalline MOF nanoparticles and the amorphous polymer halos precluded quantification of the *d*-spacing for those samples.

The dispersion of nanoparticles appears to improve slightly with increased incorporation of additional soft block. However, at extreme loadings, such as the J10 (51) sample, large agglomerations become apparent. Figure 4 presents TEM images of each Mg₂(dobdc) MMM investigated. At the length scales considered and with slightly higher resolution (Supporting Information S.4), no clear mechanical defects were observed, such as a sieve-in-cage morphology.³⁹ For the



Figure 3. Powder X-ray diffractions patterns for (A) pure polymer films and (B) films loaded with $Mg_2(dobdc)$ nanoparticles. Additional patterns for the pure nanoparticles and bulk $Mg_2(dobdc)$ are shown for comparison.

Table 2. Observed d-Spacing	of Pure	Polymers	and
Mg ₂ (dobdc)-Loaded MMMs			

	polymer <i>d</i> -spacing (Å)		
sample name	neat polymer	Mg ₂ (dobdc) MMM	
J0, J0 (28)	6.31	5.80	
J1, J1 (28)	6.03	5.77	
J5, J5 (27)	5.96	5.75	
J10, J10 (39)	5.72	5.55	

 $Ni_2(dobdc)$ samples, significantly better dispersion was observed for the J10 MMM compared to the J0 MMM (Supporting Information S.4), and similar to the Mg₂(dobdc) samples, no mechanical defects were observed. Attempts at forming continuous films of J0 with higher nanoparticle loading were unsuccessful, thereby indicating that 28 wt % is a nearexperimental maximum for the traditional lab-based solutioncasting techniques used in this study.

DMA results proved insightful for assessing the interaction between MOF nanoparticles and the polymer matrix. Figure 5 presents the tan δ response for the J0, J5, and J10 films and homologous mixed-matrix films. Unfortunately, because of thermal degradation, the J1 film yielded before reaching a temperature that corresponds with a peak in tan δ , so this sample could not be analyzed. Regardless, several clear trends are apparent from these data. First, glass transition temperatures, which correspond to the peak in tan δ , span a range of temperatures depending on copolymer composition. The T_g between J0 and J10 differed by over 200 °C, qualitatively indicating the extraordinary range of rigidity for this copolymer system. A brief discussion regarding the random nature of the copolymerization reaction is presented in Supporting Information S.5. Additionally, the pure polymers have tan δ peaks consistently greater in magnitude than those of their corresponding MMMs, indicating a better ability to dampen vibrations in the domain near the glass transition temperature.40 Interestingly, higher soft block content corresponds with a more pronounced shift in the $T_{\rm g}$ of the MMMs, qualitatively indicating a better interaction between the MOF and the copolymer. For J0, incorporation of 28 wt % $Mg_2(dobdc)$ nanoparticles results in a slight T_g shift of only



Figure 4. TEM images of film slices for Mg_2 (dobdc)-loaded MMMs. (A) J0 with 28 wt % loading, (B) J1 with 28 wt % loading, (C) J5 with 27 wt % loading, (D) J10 with 39 wt % loading, and (E) J10 with 51 wt % loading. MOF particles appear as white and the polymer appears as black.

2 °C, whereas the film with the highest soft block content, J10 (39), exhibits a shift of approximately 10 °C.

Shifts in T_g were also determined for MMMs prepared with Ni₂(dobdc) and are discussed in Supporting Information S.5.



Figure 5. DMA characterization of the tan δ response for neat polymers and Mg₂(dobdc) MMMs. Neat polymers have tan δ peaks greater in magnitude than the MMMs. Arrows are used to indicate the peak location for tan δ .

For the J0 pure polyimide, identical T_g 's of 444 °C were observed for the MMMs prepared with Ni2(dobdc) and $Mg_2(dobdc)$. However, for the J10 MMMs, the sample containing 39 wt % Mg₂(dobdc) had an observed T_g of approximately 215 °C, whereas the sample containing 20 wt % \dot{Ni}_2 (dobdc) had a T_g in the range 250–265 °C. Unfortunately, the tan δ response was extraordinarily weak for this sample, nearly within the resolution of the experiment, making the exact location of T_{g} difficult to pinpoint. Regardless, these results indicate significantly stronger interaction between Ni₂(dobdc) and J10 compared to that with J0. The origins of these increased polymer-MOF interactions are likely a combination of two factors. First, there is a higher accessible surface area for $Ni_2(dobdc)$ particles compared to that for $Mg_2(dobdc)$ particles because Ni₂(dobdc) particles are approximately 15 nm in diameter while the $Mg_2(dobdc)$ particles are approximately 200 nm in diameter.¹⁸ Second, Ni₂(dobdc) should coordinate more strongly with the polymer chains than $Mg_2(dobdc)$ according to the Irving-Williams stability order,^{18,41} so Ni would be expected to have stronger

interactions with ligands than Mg. The exact contributions from these two phenomena cannot be deconvoluted from the experiments in this study.

Shifts in T_g have classically been ascribed to the strength of the interaction between the polymer and filler.⁴² In this regard, MMMs are viewed as ternary systems that contain one phase of pure polymer, one phase of nanoparticles, and a boundary layer between the polymer and the nanoparticles. Interactions between the nanoparticle and polymer phases are often viewed analogously to those of semicrystalline polymers systems, where crystalline domains impose steric constraints on otherwise mobile, amorphous polymer chains, thereby increasing the effective T_g of the polymer.⁴³ In MMMs, these types of effects are frequently reported. For example, at 5 wt % loading, benzylamine-modified fullerenes result in a 14 °C shift in the T_g of the polyimide Matrimid,⁴⁴ at 50 wt % loading, zeolites 4Å and 5A result in 4 and 6 °C shifts, respectively, in the T_{σ} of poly(ether sulfone),45 and at approximately 36 vol % loading, carbon molecular sieves result in 5 and 15 $^{\circ}$ C shifts in the T_{σ} for Ultem and Matrimid polyimides, respectively. While not exclusive to all systems, stronger polymer-nanoparticle interactions are frequently identified as a primary reason for so-called "pore-blocking" effects, where the rigidified polymer chain surrounding the nanoparticle prevents efficient diffusion of gas molecules through porous materials, thereby resulting in substantial decreases in permeability.³⁹ For our systems, we observed significant changes to the $T_{\rm g}$ for the MMMs compared to those of the neat polymers, especially for the ether-containing copolymers and for Ni2(dobdc)-containing systems, a result that suggests chain rigidification. Interestingly, we observed, in all cases, increases in permeability for the MMMs compared to the neat polymers, indicating that the porosity in $M_2(dobdc)$ was still accessible.

3.2. Mechanical Properties of Pure Polymers and Mixed-Matrix Membranes. In principle, MMMs are an attractive platform of materials because they unite the transport performance of inorganic materials with the processability of polymers. However, a polymer with excellent mechanical properties will not necessarily maintain these properties once formed into a composite, thereby necessitating the quantitative assessment of mechanical properties for MMMs. Unfortunately,



Figure 6. Stress-strain curves for (A) neat polymers and (B) Mg₂(dobdc) MMMs, performed at room temperature and a strain rate of 1.3 mm/s.

the literature contains abundant data on high-performance MMMs with few reports on quantitative mechanical properties. Within the small subcategory of MMMs with reported mechanical properties, even fewer properties have been determined using standard methods such as those prescribed by the American Society of Testing and Materials (ASTM).

To more clearly show quantitative comparisons of mechanical properties, we have determined static stress—strain curves following the ASTM D1708-13 method.³¹ Static stress—strain curves for the neat polymers are presented in Figure 6A. Addition of soft block content has a profound effect on the mechanical properties of these materials, as observed by the reduction in ultimate strength and the increase in elongation at break with increasing soft block content. For example, the ultimate strength decreases from 71 MPa for J0 to 35 MPa for J10, and the elongation at break increases from 50% for J0 to 302% for J10. These changing property sets are a consequence of incorporating rubbery subunits into the polymer backbone and result in tougher polymer films.

Figure 6B clearly shows the consequence of adding $Mg_2(dobdc)$ nanoparticles to these polymers. At approximately 30 wt % $Mg_2(dobdc)$ loadings, J0, J1, and J5 all undergo brittle failure, breaking sharply before plastic deformation. However, in contrast, at sufficiently high polyether content, such as in the J10 (39) sample, plastic deformation of the MMM can be achieved before the sample yields. The elongation at break for J10 (39) is approximately 5.5%, which is starting to approach that of rigid BTDA-containing polyimides, such as BTDA-4-BDAF, BTDA-MDA, and BTDA-MPD/MDA, which have elongations at break of approximately 9–10%.⁴⁶ Still, this MMM has elongations at break far below that of commercially available polymers, even the BTDA-containing polyimide, Matrimid, which has an elongation at break of 48%.⁴⁶

Incorporation of Ni₂(dobdc) nanoparticles in the pure polyimide, J0, also strongly reduces the strength and ductility of the composite membranes. However, MMMs formed with 21 wt % Ni₂(dobdc) nanoparticles and J10 exhibit ductilities comparable to several commercially available polymers that are used for membrane-based gas separations today. Tensile tests for the Ni₂(dobdc)-containing MMMs are presented in the Supporting Information (SI S.6). A global comparison of the strength and ductility for samples considered in this study, polyimides reported in the literature, and commercially available polymer membrane materials is presented in Figure 7.46 Note that these results are sensitive to strain rates and sample measurement temperatures, so references have been chosen for experiments believed to have been performed at or near room temperature and for strain rates consistent with ASTM tests for these polymer systems. These data show that the range of strength and ductility for the copolymer system considered in this study partially spans the range of mechanical properties accessible to polymers used industrially for forming gas separation membranes. Furthermore, MMMs formed from Mg₂(dobdc) nanoparticles, which have effective particle diameters of approximately 200 nm, were significantly weaker and more brittle than their pure polymer analogues. Similar conclusions are drawn for the MMMs formed from J0 and Ni₂(dobdc) nanoparticles, which have effective particle diameters of approximately 18 nm. However, the J10 sample with 21 wt % Ni₂(dobdc) maintained strength and ductility, undergoing plastic deformation and exhibiting an elongation at break of 43%. These results indicate that polymer flexibility, as controlled by high polyether content and small nanoparticle

Neat Polymers Literature Data Mg₂(dobdc) MMMs -0-* Commercial Membranes - A- Ni (dobdc) MMMs Yield Strength (MPa) Strong -★Polycarbonate Matrimid[®] ★TB-BisA-PC Cellulose Acetate * ★ Polysulfone .15 J0 (20) *PPO J10 (21) J10 J10 (39) J5 (27) Brittle Ductile ----10 10 100

Elongation at Break (%)

Figure 7. (A) Comparison of film strength and ductility for neat polymers (filled squares), MMMs (open squares), polyimides (circles), and commercially available polymer membranes (stars). TB-BisA-PC stands for tetrabromobisphenol-A polycarbonate, and PPO stands for poly(phenylene oxide).

sizes, promotes the formation of MMMs that are more mechanically robust. Moreover, the J10 (21) sample is more ductile than cellulose acetate, a polymer commonly deployed for membrane-based separations, and this sample has a comparable yield strength to other polymers used for commercial membrane-based separations. Additional mechanical property data on sample modulus and toughness are presented in the Supporting Information (S.7).

3.3. Gas Transport Properties. Gas transport properties were determined for H_2 , N_2 , CH_4 , and CO_2 . To provide a comparison between our results and those of pure polymers in the literature, Robeson Upper Bound plots are presented for H_2/N_2 , H_2/CH_4 , CO_2/N_2 , and CO_2/CH_4 separation in parts A, B, C, and D, respectively, of Figure 8.⁴ For all separations considered, addition of polyether content results in a decrease in permeability for the copolymers. These changes in transport properties correlate with reductions in the *d*-spacing determined from powder diffraction analysis. Furthermore, the upper bound fronts presented in Figure 8 are populated by diffusion selective polymers, ^{4,47} so the reduction of T_g upon addition of polyether indicates increased flexibility of the polymer backbone that would result in a weaker size-sieving ability for the ether-containing polymers.

Addition of M₂(dobdc) nanoparticles always resulted in an increase in gas permeability. These results suggest that the porosity of $M_2(dobdc)$ is accessible to the permeating gases, similar to MMMs prepared from Mg₂(dobdc) with other glassy polymers, such 6FDA-DAM (DAM = diaminomesitylene), but in contrast to pore-blocking mechanisms that have been reported for rubbery cross-linked poly(ethylene oxide) and polydimethylsiloxane membranes.¹⁷ In addition to increasing permeability, for certain gas pairs, increases in selectivity were also observed. Interestingly, all MMMs prepared from J0 and J1 resulted in decreased selectivity, whereas, in the case of hydrogen separations, samples prepared from J5 and J10 with $Mg_2(dobdc)$ resulted in increases in selectivity with increasing MOF loading. Decreases in selectivity for J0 and J1 samples are consistent with the formation of nonselective defects between MOF nanoparticles and the rigid polymer matrix. However, for the more flexible samples J5 and J10, our results suggest that



Figure 8. Upper Bound comparison for (A) H_2/N_{22} (B) H_2/CH_4 , (C) CO_2/N_2 , and (D) CO_2/CH_4 separation. Neat polymers are presented as filled squares and MMMs are presented as open symbols. The J10 (51) film is presented as an open square with a center dot and literature data from ref 4 are presented as gray circles. Multiple data points are plotted to highlight the effect of pressure between approximately 0.33 and 65 bar on H_2 separations, but to avoid data complications from plasticization, only data taken at approximately 1 bar is plotted for separations involving CO_2 . For H_2 separations, pure-gas selectivity increases with increasing pressure. MMMs prepared from Ni₂(dobdc) are presented as open purple triangles. Arrows are drawn to connect samples prepared from identical polymer matrixes.

these defects are sealed, thereby resulting in selective permeation of small molecules. The full set of permeation data for samples considered in this study is presented in Supporting Information S.8. Additionally, plasticization pressure behavior for all samples and hysteresis effects for neat polymers and Mg₂(dobdc) MMMs are presented in Supporting Information S.8. These results indicate an increased resistance to CO₂ plasticization and a decrease in CO₂ hysteresis effects for the MMMs compared to the neat polymers. Moreover, Ni₂(dobdc) particles have a greater effect on mitigating plasticization behavior than Mg₂(dobdc) particles, similar to our previous findings.^{18,19}

Additional permeation experiments were performed on the J10 (39) sample to investigate the influence of open metal sites on permeability and selectivity (Supporting Information S.9). For these experiments, the MMM was saturated with water at room temperature, placed in the permeation cell, and held under vacuum for 3 days to extract loosely bound water from the MMM. Because water cannot be removed from the open

metal sites of $M_2(dobdc)$ without activation temperatures above 100 °C,⁴⁸ and because the gas molecules considered in this study are not expected to displace water bound to the metal sites,⁴⁹ this procedure effectively blocks the open metal sites from interactions with weakly binding gaseous penetrants. At 1 bar, H_2/CH_4 selectivity increased slightly from the pure polymer to the MMM, changing from 6.8 ± 0.8 to 8.0 ± 0.5 . The H_2 permeability also increased slightly from 13 ± 2 to 20 ± 1 Barrer. These relatively minor changes in transport properties contrast with those of the fully activated J10 (39) sample, which displayed an H_2/CH_4 selectivity of 10.3 ± 0.9 and H_2 permeability of 42 ± 6 Barrer. Therefore, improvements in permeability and selectivity are most strongly influenced by access to the open metal sites in these MMMs.

Variants of $M_2(dobdc)$ achieve their separation performance because of selective adsorption of more strongly polarizable molecules. This type of separation performance provides the molecular basis for the outstanding adsorption-based selectivities of $M_2(dobdc)$ for CO₂ and olefin/paraffin separations.^{14,15}



Figure 9. Relative changes in permeability, effective diffusivity, and effective solubility for (A) J10 (39) and (B) J10 (51) determined for a transmembrane pressure of 1 bar and a temperature of 35 $^{\circ}$ C.

However, for the MMMs considered in this study, the most significant improvements to membrane transport performance were observed for H₂ separations, which, based on the weakly adsorbing nature of H₂ compared to those of N₂, CH₄, and CO₂, is counterintuitive to the adsorption-based mechanism for selective adsorption of $M_2(dobdc)$. To investigate the origins of this unusual behavior, changes in permeability, diffusion, and effective sorption were approximated for J10, J10 (39), and J10 (51). Diffusion coefficients were estimated by the classic timelag method,³⁰ and sorption coefficients were estimated by dividing permeability by the time-lag diffusion. Of course, MOFs containing open metal sites, such as M2(dobdc), could potentially act as an adsorptive filler, thereby significantly lengthening the apparent time-lag.⁵⁰ Nevertheless, these results provide a useful qualitative comparison for analyzing transport properties in the MMMs considered in this study.

Comparing the contributions of diffusivity and solubility to permeability helps elucidate the mechanism of transport in M₂(dobdc) MMMs. For J10, addition of 39 wt % Mg₂(dobdc) increases H₂ permeability by 230%, while addition of 51 wt % $Mg_2(dobdc)$ increases it by 920%. These increases are significantly higher than those observed for the other gases measured, where the relative changes in permeability, which are presented in Figure 9, increase in the following order: $H_2 > N_2$ ~ $CH_4 > CO_2$. Interestingly, permeability increases less for more strongly adsorbing penetrants. These trends closely correlate with the isosteric heats of adsorption for the gases considered. At the open metal sites, bulk $Mg_2(dobdc)$ has isosteric heats of adsorption of -10.3, 51, -21, 52, -18.6, 53, and -42 kJ/mol,⁵⁴ for H₂, N₂, CH₄, and CO₂, respectively, although adsorption at secondary binding sites is considerably lower.¹⁴ Additionally, the changes in solubility correlated very well with the relative uptake expected at low pressures for bulk $Mg_2(dobdc)$. At 40 °C and 1 bar, $Mg_2(dobdc)$ has an uptake of 0.65 mmol/g for N_2 , ⁵⁴ 1.13 mmol/g for CH_4 , ⁵⁵ and 7.68 mmol/g for CO₂.⁵⁴ For the MMMs considered here, the most pronounced increase in solubility occurs for CO₂, followed by that of CH₄ and N₂ (Figure 9). Furthermore, changes in diffusion coefficients are inversely related to changes in

solubility. Compared to neat J10, the effective diffusivity for N_2 in J10 (51) increases by 320% compared to an increase in solubility of only 40%. In contrast, CO₂ diffusivity increases by only 50% and solubility increases by 220%. These results suggest that the strong binding of the open metal site promote increased permeation based on solubility effects, but correspondingly, result in decreased penetrant diffusivities. Unfortunately, the high diffusion rates of H₂ in these MMMs precluded analyzing solubility and diffusivity for this gas. However, the trends observed for N₂, CH₄, and CO₂ suggest that the relative change in H₂ permeation is most pronounced because of its weak interaction with the open metal sites and the resulting large increase in diffusion due to the porous architecture of Mg₂(dobdc). For the J10 polymer and MMMs, static adsorption isotherms could not be reliably determined due to the slow diffusion of gases into these samples. Nevertheless, after sufficient equilibration time, static adsorption coefficients were within the uncertainty of those measured by the time-lag method, thereby supporting the use of the time-lag approach for estimating transport properties in these MMMs (Supporting Information S.10).

4. CONCLUSIONS

This study demonstrates the importance of tuning the physical properties of a polymer to reduce nonselective defects in mixed-matrix membranes (MMMs). In particular, high loadings of up to 51 wt % of nanoparticles of a metal-organic framework (MOF) with open metal sites, Mg₂(dobdc), could be formed into a continuous film using a copolymer synthesized from a hard block imide, 6FDA-durene, and a soft block polyether. Addition of $M_2(dobdc)$ resulted in a densification of the MMM. However, significant increases in permeability for H₂, N₂, CH₄, and CO₂ were observed upon incremental addition of Mg2(dobdc) nanoparticles, indicating the important role of gas transport through the porous MOF architecture. Access to the open metal sites resulted in a tradeoff in changes to fundamental transport parameters: penetrants that interact more strongly with the open metal sites showed reduced relative changes in diffusivity compared to weaker interacting diluents. Improvements to the Robeson Upper Bound, therefore, were more pronounced for separations governed by diffusion selectivity, such as H_2/CH_4 and H_2/N_2 separations, compared to those separations governed by diffusion and solubility selectivity, such as CO_2/CH_4 and CO_2/N_2 separations. Improvements to transport performance were countered by increased weakness and brittleness for MMMs formed with Mg₂(dobdc). In contrast, Ni₂(dobdc) nanoparticles, which were significantly smaller than the Mg₂(dobdc) nanoparticles, could be used to form stronger and more ductile films, some of which exhibited mechanical robustness comparable to commercially available polymers used in membrane applications today. However, high contents of the soft polyether block were needed to achieve these mechanical properties, which adversely affected transport behavior. This work demonstrates the importance of forming a compatible MOF-polymer interface to address issues concerning nonselective defects and mechanical embrittlement typically found in MOF-containing MMMs.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemma-ter.7b02908.

NMR characterization of synthesized polymers; viscosity of polymer solutions; DSC study of J10 copolymer; TEM characterization for $Mg_2(dobdc)$ and $Ni_2(dobdc)$ mixedmatrix films; DMA results for mixed-matrix films and a comment on polymer miscibility; tensile testing characteristics for $Ni_2(dobdc)$ mixed-matrix films; additional mechanical testing characteristics; full permeation characterization data points for neat polymers and MMMs; mixed-matrix properties for water-laden film; static versus time-lag sorption calculations (PDF)

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Notes

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REFERENCES

(1) Baker, R. W.; Low, B. T. Gas separation membrane materials: A perspective. *Macromolecules* **2014**, *47*, 6999–7013.

(2) Baker, R. W.; Lokhandwala, K. Natural gas processing with membranes: An overview. *Ind. Eng. Chem. Res.* 2008, 47, 2109–2121.
(3) Wijmans, J. G.; Baker, R. W. The solution-diffusion model: A review. *J. Membr. Sci.* 1995, 107, 1–21.

(4) Robeson, L. M. The upper bound revisited. J. Membr. Sci. 2008, 320, 390-400.

(5) Chung, T.-S.; Jiang, L. Y.; Li, Y.; Kulprathipanja, S. Mixed matrix membranes (MMMs) comprising organic polymers with dispersed inorganic fillers for gas separation. *Prog. Polym. Sci.* **2007**, *32*, 483–507.

(6) Zornoza, B.; Tellez, C.; Coronas, J.; Gascon, J.; Kapteijn, F. Metal organic framework based mixed matrix membranes: An increasingly important field of research with a large application potential. *Microporous Mesoporous Mater.* **2013**, *166*, 67–78.

(7) Vu, D. Q.; Koros, W. J.; Miller, S. J. Mixed matrix membranes using carbon molecular sieves: I. Preparation and experimental results. *J. Membr. Sci.* **2003**, *211*, 311–334.

(8) Vu, D. Q.; Koros, W. J.; Miller, S. J. Mixed matrix membranes using carbon molecular sieves: II. Modeling permeation behavior. *J. Membr. Sci.* **2003**, *211*, 335–348.

(9) Bernardo, P.; Drioli, E.; Golemme, G. Membrane gas separation: A review/state of the art. *Ind. Eng. Chem. Res.* **2009**, *48*, 4638–4663.

(10) Zhang, C.; Dai, Y.; Johnson, J. R.; Karvan, O.; Koros, W. J. High performance ZIF-8/6FDA-DAM mixed matrix membrane for propylene/propane separations. *J. Membr. Sci.* **2012**, 389, 34–42.

(11) Zhang, C.; Lively, R. P.; Zhang, K.; Johnson, J. R.; Karvan, O.; Koros, W. J. Unexpected molecular sieving properties of zeolitic imidazolate framework-8. *J. Phys. Chem. Lett.* **2012**, *3*, 2130–2134.

(12) Kwon, H. T.; Jeong, H.-K. In situ synthesis of thin zeoliticimidazolate framework ZIF-8 membranes exhibiting exceptionally high propylene/propane separation. *J. Am. Chem. Soc.* **2013**, *135*, 10763– 10768.

(13) Pan, Y.; Lai, Z. Sharp separation of C_2/C_3 hydrocarbon mixtures by zeolitic imidazolate framework-8 (ZIF-8) membranes synthesized in aqueous solutions. *Chem. Commun.* **2011**, 47 (37), 10275–10277.

(14) Queen, W. L.; Hudson, M. R.; Bloch, E. D.; Mason, J. A.; Gonzalez, M. I.; Lee, J. S.; Gygi, D.; Howe, J. D.; Lee, K.; Darwish, T. A.; James, M.; Peterson, V. K.; Teat, S. J.; Smit, B.; Neaton, J. B.; Long, J. R.; Brown, C. M. Comprehensive study of carbon dioxide adsorption in the metal–organic frameworks M_2 (dobdc) (M = Mg, Mn, Fe, Co, Ni, Cu, Zn). *Chem. Sci.* **2014**, *5*, 4569–4581.

(15) Geier, S. J.; Mason, J. A.; Bloch, E. D.; Queen, W. L.; Hudson, M. R.; Brown, C. M.; Long, J. R. Selective adsorption of ethylene over ethane and propylene over propane in the metal-organic frameworks

M₂(dobdc) (M = Mg, Mn, Fe, Co, Ni, Zn). *Chem. Sci.* **2013**, *4*, 2054–2061.

(16) Caskey, S. R.; Wong-Foy, A. G.; Matzger, A. J. Dramatic tuning of carbon dioxide uptake via metal substitution in a coordination polymer with cylindrical pores. *J. Am. Chem. Soc.* **2008**, *130*, 10870–10871.

(17) Bae, T.-H.; Long, J. R. CO_2/N_2 separations with mixed-matrix membranes containing $Mg_2(dobdc)$ nanocrystals. *Energy Environ. Sci.* **2013**, *6*, 3565–3569.

(18) Bachman, J. E.; Smith, Z. P.; Li, T.; Xu, T.; Long, J. R. Enhanced ethylene separation and plasticization resistance in polymer membranes incorporating metal-organic framework nanocrystals. *Nat. Mater.* **2016**, *15*, 845–9.

(19) Bachman, J. E.; Long, J. R. Plasticization-resistant $Ni_2(dobdc)/$ polyimide composite membranes for the removal of CO_2 from natural gas. *Energy Environ. Sci.* **2016**, *9*, 2031–2036.

(20) Ordoñez, M. J. C.; Balkus, K. J., Jr; Ferraris, J. P.; Musselman, I. H. Molecular sieving realized with ZIF-8/Matrimid® mixed-matrix membranes. J. Membr. Sci. 2010, 361 (1–2), 28–37.

(21) Mahdi, E. M.; Tan, J. C. Dynamic molecular interactions between polyurethane and ZIF-8 in a polymer-MOF nanocomposite: Microstructural, thermo-mechanical and viscoelastic effects. *Polymer* **2016**, *97*, 31–43.

(22) Mahdi, E. M.; Tan, J.-C. Mixed-matrix membranes of zeolitic imidazolate framework (ZIF-8)/Matrimid nanocomposite: Thermomechanical stability and viscoelasticity underpinning membrane separation performance. *J. Membr. Sci.* **2016**, *498*, 276–290.

(23) Smith, S. J.; Lau, C. H.; Mardel, J. I.; Kitchin, M.; Konstas, K.; Ladewig, B. P.; Hill, M. R. Physical aging in glassy mixed matrix membranes; tuning particle interaction for mechanically robust nanocomposite films. *J. Mater. Chem. A* **2016**, *4*, 10627–10634.

(24) Struik, L. C. E. *Physical aging in amorphous polymers and other materials;* Elsevier Scientific Pub. Co.: Amsterdam, The Netherlands, 1978.

(25) Tanaka, K.; Okano, M.; Toshino, H.; Kita, H.; Okamoto, K.-I. Effect of methyl substituents on permeability and permselectivity of gases in polyimides prepared from methyl-substituted phenylenediamines. *J. Polym. Sci., Part B: Polym. Phys.* **1992**, *30*, 907–914.

(26) Wu, S. Phase structure and adhesion in polymer blends: A criterion for rubber toughening. *Polymer* **1985**, 26 (12), 1855–1863. (27) Ghosh, M. K.; Mital, K. L. *Polyimides: Fundamentals and*

Applications; Marcel: New York, 1996. (28) Lin, H.; Freeman, B. D. Springer handbook: Permeation and

diffusion; Czichos, H., Saito, T., Smith, L., Eds.; Springer: New York, 2006; pp 371–387.

(29) Smith, Z. P.; Tiwari, R. R.; Dose, M. E.; Gleason, K. L.; Murphy, T. M.; Sanders, D. F.; Gunawan, G.; Robeson, L. M.; Paul, D. R.; Freeman, B. D. Influence of diffusivity and sorption on helium and hydrogen separations in hydrocarbon, silicon, and fluorocarbon-based polymers. *Macromolecules* **2014**, *47*, 3170–3184.

(30) Frisch, H. L. The time lag in diffusion. J. Phys. Chem. 1957, 61, 93-95.

(31) D1708-13. A. S., Standard Test Method for Tensile Properties of Plastics by Use of Microtensile Specimens. ASTM International: West Conshohocken, PA, 2013.

(32) Miyata, S.; Sato, S.; Nagai, K.; Nakagawa, T.; Kudo, K. Relationship between gas transport properties and fractional free volume determined from dielectric constant in polyimide films containing the hexafluoroisopropylidene group. *J. Appl. Polym. Sci.* **2008**, *107*, 3933–3944.

(33) Huertas, R. M.; Doherty, C. M.; Hill, A. J.; Lozano, A. E.; de Abajo, J.; de la Campa, J. G.; Maya, E. M. Preparation and gas separation properties of partially pyrolyzed membranes (PPMs) derived from copolyimides containing polyethylene oxide side chains. *J. Membr. Sci.* **2012**, 409–410, 200–211.

(34) Aroon, M. A.; Ismail, A. F.; Matsuura, T.; Montazer-Rahmati, M. M. Performance studies of mixed matrix membranes for gas separation: A review. *Sep. Purif. Technol.* **2010**, *75*, 229–242.

(35) Kim, S.; Pechar, T. W.; Marand, E. Poly(imide siloxane) and carbon nanotube mixed matrix membranes for gas separation. *Desalination* **2006**, *192*, 330–339.

(36) Lin, H.; Freeman, B. D. Gas solubility, diffusivity and permeability in poly (ethylene oxide). *J. Membr. Sci.* 2004, 239, 105–117.

(37) Gómez Ribelles, J. L.; Salmerón Sanchez, M.; de la Osa, L. T.; Krakovský, I. Thermal transitions in α,ω -diamino terminated poly-(oxypropylene)-block-poly(oxyethylene)-block-poly(oxypropylene) aqueous solutions and their epoxy networks. *J. Non-Cryst. Solids* **2005**, 351, 1254–1260.

(38) Hellums, M.; Koros, W.; Husk, G.; Paul, D. Fluorinated polycarbonates for gas separation applications. *J. Membr. Sci.* **1989**, *46*, 93–112.

(39) Vinh-Thang, H.; Kaliaguine, S. Predictive models for mixedmatrix membrane performance: A review. *Chem. Rev.* 2013, 113, 4980–5028.

(40) Menard, K. P. Dynamic mechanical analysis: a practical introduction; CRC Press: Boca Raton, FL, 2008.

(41) Irving, H.; Williams, R. J. P. 637. The stability of transition-metal complexes. *J. Chem. Soc.* **1953**, 3192–3210.

(42) Moore, T. T.; Mahajan, R.; Vu, D. Q.; Koros, W. J. Hybrid membrane materials comprising organic polymers with rigid dispersed phases. *AIChE J.* **2004**, *50*, 311–321.

(43) Michaels, A. S.; Vieth, W. R.; Barrie, J. A. Diffusion of gases in polyethylene terephthalate. *J. Appl. Phys.* **1963**, *34*, 13–20.

(44) Chung, T.; Chan, S. S.; Wang, R.; Lu, Z.; He, C. Characterization of permeability and sorption in Matrimid/C60 mixed matrix membranes. *J. Membr. Sci.* **2003**, *211*, 91–99.

(45) Li, Y.; Chung, T.-S.; Cao, C.; Kulprathipanja, S. The effects of polymer chain rigidification, zeolite pore size and pore blockage on polyethersulfone (PES)-zeolite A mixed matrix membranes. *J. Membr. Sci.* **2005**, *260*, 45–55.

(46) Ellis, B.; Smith, R. Polymers: a property database; CRC Press: Boca Raton, FL, 2008.

(47) Freeman, B. D. Basis of permeability/selectivity tradeoff relations in polymeric gas separation membranes. *Macromolecules* **1999**, *32*, 375–380.

(48) Tan, K.; Zuluaga, S.; Gong, Q.; Canepa, P.; Wang, H.; Li, J.; Chabal, Y. J.; Thonhauser, T. Water reaction mechanism in metal organic frameworks with coordinatively unsaturated metal ions: MOF-74. *Chem. Mater.* **2014**, *26*, 6886–6895.

(49) Tan, K.; Zuluaga, S.; Gong, Q.; Gao, Y.; Nijem, N.; Li, J.; Thonhauser, T.; Chabal, Y. J. Competitive coadsorption of CO_2 with H_2O , NH_3 , SO_2 , NO, NO_2 , N_2 , O_2 , and CH_4 in M-MOF-74 (M = Mg, Co, Ni): The role of hydrogen bonding. *Chem. Mater.* **2015**, *27*, 2203–2217.

(50) Paul, D.; Kemp, D. The diffusion time lag in polymer membranes containing adsorptive fillers. J. Polym. Sci., Polym. Symp. **1973**, 41, 79–93.

(51) Zhou, W.; Wu, H.; Yildirim, T. Enhanced H_2 adsorption in isostructural metal–organic frameworks with open metal sites: Strong dependence of the binding strength on metal ions. *J. Am. Chem. Soc.* **2008**, 130, 15268–15269.

(52) Valenzano, L.; Civalleri, B.; Chavan, S.; Palomino, G. T.; Areán, C. O.; Bordiga, S. Computational and experimental studies on the adsorption of CO, N_{2j} and CO₂ on Mg-MOF-74. *J. Phys. Chem. C* **2010**, *114*, 11185–11191.

(53) Mason, J. A.; Veenstra, M.; Long, J. R. Evaluating metal-organic frameworks for natural gas storage. *Chem. Sci.* **2014**, *5*, 32–51.

(54) Mason, J. A.; Sumida, K.; Herm, Z. R.; Krishna, R.; Long, J. R. Evaluating metal-organic frameworks for post-combustion carbon dioxide capture via temperature swing adsorption. *Energy Environ. Sci.* **2011**, *4*, 3030–3040.

(55) Herm, Z. R.; Krishna, R.; Long, J. R. CO_2/CH_4 , CH_4/H_2 and $CO_2/CH_4/H_2$ separations at high pressures using $Mg_2(dobdc)$. *Microporous Mesoporous Mater.* **2012**, *151*, 481.