

Highly Permeable Benzotriptycene-Based Polymer of Intrinsic Microporosity

Ian Rose,[†] Mariolino Carta,[†] Richard Malpass-Evans,[†] Maria-Chiara Ferrari,[‡] Paola Bernardo,[§] Gabriele Clarizia,[§] Johannes C. Jansen,[§] and Neil B. McKeown^{*,†}

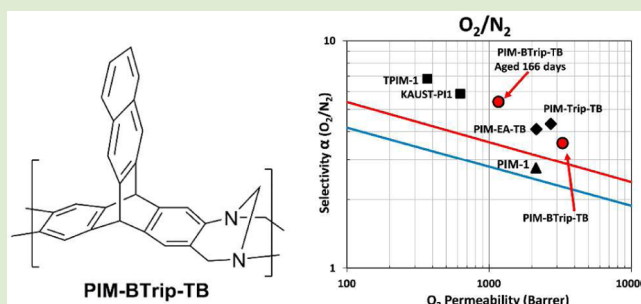
[†]EaStCHEM School of Chemistry, University of Edinburgh, David Brewster Road, Edinburgh EH9 3FJ, U.K.

[‡]Institute for Materials and Processes, School of Engineering, The University of Edinburgh, Mayfield Road, Edinburgh EH9 3JL, U.K.

[§]Institute on Membrane Technology, ITM-CNR, c/o University of Calabria, Via P. Bucci 17/C, 87036 Rende (CS), Italy

Supporting Information

ABSTRACT: A novel polymer of intrinsic microporosity (PIM) was prepared from a diaminobenzotriptycene monomer using a polymerization reaction based on Tröger's base formation. The polymer (PIM-BTrip-TB) demonstrated an apparent Brunauer, Emmet, and Teller (BET) surface area of $870 \text{ m}^2 \text{ g}^{-1}$, good solubility in chloroform, excellent molecular mass, high inherent viscosity and provided robust thin films for gas permeability measurements. The polymer is highly permeable (e.g., $P_{\text{H}_2} = 9980$; $P_{\text{O}_2} = 3290$ Barrer) with moderate selectivity (e.g., $P_{\text{H}_2}/P_{\text{N}_2} = 11.0$; $P_{\text{O}_2}/P_{\text{N}_2} = 3.6$) so that its data lie over the 2008 Robeson upper bounds for the H_2/N_2 , O_2/N_2 , and H_2/CH_4 gas pairs and on the upper bound for CO_2/CH_4 . On aging, the polymer demonstrates a drop in permeability, which is typical for ultrapermeable polymers, but with a significant increase in gas selectivities (e.g., $P_{\text{O}_2} = 1170$ Barrer; $P_{\text{O}_2}/P_{\text{N}_2} = 5.4$).



The preparation of new polymeric membranes for gas separation is receiving increasing attention, by both academia and industry,¹ as a result of their potential for a number of important separations, including O_2/N_2 ² for the production of oxygen-enriched or depleted air, CO_2/CH_4 ³ for natural gas enrichment, CO_2/N_2 ⁴ for carbon capture, and H_2/N_2 and H_2/CO_2 ⁵ for the recovery and production of hydrogen.⁶ The performance of membranes for gas separation is typically evaluated by measuring the permeability of single species (P_x and P_y) and calculating the ideal selectivity of one component of a gas pair relative to the other ($\alpha_{xy} = P_x/P_y$). It was found that polymers suffer a trade-off relationship between these two values so that highly selective polymers have low permeability and vice versa. This relationship was empirically quantified by Robeson⁷ and then theoretically explained by Freeman.⁸ Following these studies, it was suggested that, to surpass the Robeson upper bounds, it was desirable to prepare polymers with higher internal free volume, by increasing interchain distances, and with enhanced backbone rigidity to improve selectivity via molecular sieving. Polymers of intrinsic microporosity (PIMs), first reported in 2004,⁹ in which a highly rigid and contorted macromolecular structure ensures high free volume, conform to this design strategy.¹⁰ Recently, we reported a new class of PIMs prepared using the efficient formation of the highly rigid and contorted bicyclic diamine called Tröger's base (PIM-TB).¹¹ When the polymerization was performed using a diamine monomer containing a bridged bicyclic structure, such as 2,6(7)-diamino-9,10-dimethyletha-

noanthracene, a highly rigid polymer was prepared (PIM-EA-TB, Figure 1). This polymer demonstrates very efficient molecular sieving properties, showing very high gas permeability and good selectivity so that its data surpass the 2008 upper bounds for important gas pairs such as O_2/N_2 , H_2/N_2 , H_2/CH_4 , and H_2/CO_2 .

Recently we showed that the replacement of the ethanoanthracene unit (PIM-EA-TB) with triptycene (PIM-Trip-TB, Figure 1) resulted in increased permeability for all of the tested gases.¹² We attributed this improvement to the propeller-like structure of the triptycene unit, which provides additional interchain distance, making it a very useful component for both porous polymers¹³ and PIMs.^{14,15} In an earlier study, Sydlik et al.¹⁶ showed that the replacement of triptycene with benzotriptycene enhanced free volume within a series of polyimides due to what was defined as benzotriptycene's greater "Internal Molecular Free Volume"¹⁷ relative to that of triptycene. Hence we anticipated that using benzotriptycene in place of ethanoanthracene or triptycene would further enhance the gas permeability of the PIM-TB series as has been demonstrated recently by Alghunaimi et al. for a polyimide.¹⁸ In this paper, we report the synthesis, characterization, and gas

Received: July 1, 2015

Accepted: August 12, 2015

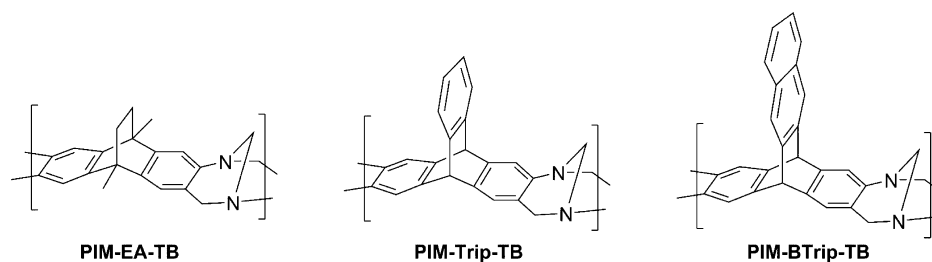
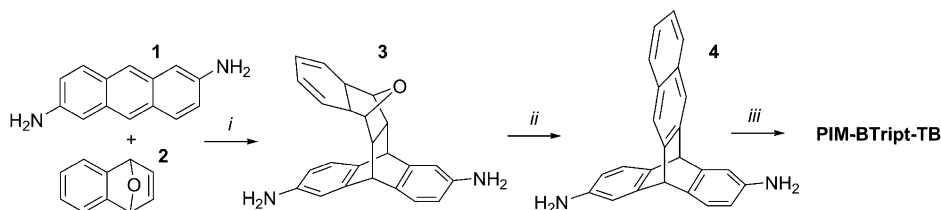


Figure 1. Structures of PIM-EA-TB,¹³ PIM-Trip-TB,¹² and PIM-BTrip-TB.

Scheme 1. Reagents and Conditions: (i) DMF, μw Irradiation, 250 °C; (ii) HClO_4 , Reflux, NaOH; (iii) Dimethoxymethane, TFA, rt



permeability studies of PIM-BTrip-TB (Figure 1) and confirm the validity of this prediction.

The synthesis of the required 2,6-diaminobenzotriptycene monomer 4 (Scheme 1) was performed using a slightly modified version of the method reported by Sydlik et al.¹⁶ involving the Diels–Alder reaction between 2,6-diaminoanthracene 1 and 1,4-dihydro-1,4-epoxynaphthalene 2 to obtain the adduct 3 followed by its dehydration with perchloric acid. The only significant difference between our method and that of Sydlik et al.¹⁶ was the use of microwave irradiation for the Diels–Alder step, which allowed us to obtain the adduct 3 rapidly (2.5 h instead of 4 days) and in higher yield (90%).

An advantage of this synthetic route is that it allows the formation of the final monomer as a single product in contrast to the monomer synthesis procedure used previously for PIM-EA-TB and PIM-Trip-TB, via nitration of the respective hydrocarbon, which results in an equal mixture of the 2,6(7)-diamino regioisomers. We recently demonstrated that the use of a single isomer benefits the polymerization of a PIM, improving the physical properties of the films.¹⁹

PIM-BTrip-TB was prepared from a polymerization reaction, optimized for TB formation,¹¹ by the addition of monomer 4 to a solution of five molar equivalents of dimethoxymethane in trifluoroacetic acid (TFA).

The complete solubility of the product in chloroform permitted characterization by NMR, gel permeation chromatography (GPC), which indicated a weight-average molecular mass of $103 \times 10^3 \text{ g mol}^{-1}$ as compared to polystyrene standards (Figure S1), and viscosity measurements, which showed an inherent viscosity of $73 \text{ cm}^3 \text{ g}^{-1}$, a result that is consistent with previously reported values obtained from solutions of film-forming PIMs.¹⁹ The physical properties are summarized in Table S1. A model of the PIM-BTrip-TB (Figure 2) shows that its macromolecular structure is contorted in three dimensions which, combined with its high rigidity, would be expected to result in inefficient packing of the polymer chains in the solid state and, therefore, would generate intrinsic microporosity. This contorted structure also minimized cohesive interactions which presumably account for the solubility of the polymer despite its extreme rigidity. The N_2 adsorption isotherm acquired at 77 K (Figure S2) confirms its

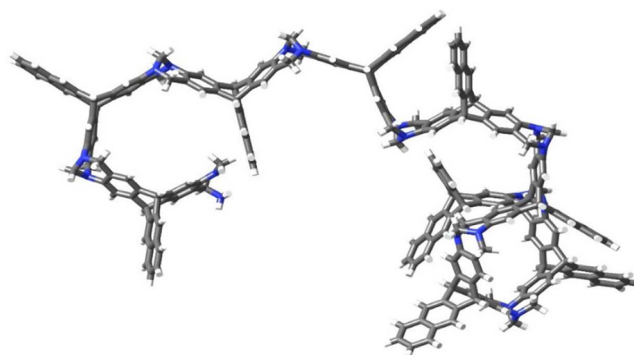


Figure 2. Molecular model of a fragment of PIM-BTrip-TB (made with Spartan 10 vVersion 1.1.0; Wave Function Inc., Irvine, CA, USA).

microporous structure and allows an apparent BET surface area of $870 \text{ m}^2 \text{ g}^{-1}$ to be calculated. This value is similar to that of PIM-Trip-TB but is significantly less than that found for PIM-EA-TB (Table S1). CO_2 adsorption data for PIM-BTrip-TB show that 3.0 mmol g^{-1} is adsorbed at 1 bar/273 K (Figure S3), which is greater than the 2.1 mmol g^{-1} reported for PIM-Trip-TB.¹² Thermogravimetric analysis (TGA) of PIM-BTrip-TB indicated a similar thermal stability to that of PIM-Trip-TB but enhanced as compared to that of PIM-EA-TB, which appears to suffer from the loss of ethylene ($\sim 10\%$ mass) via a retro-Diels–Alder reaction commencing at 325 °C (Figure S4).

Slow evaporation (over 5 days) of a solution of PIM-BTrip-TB in chloroform (700 mg in 18 mL) cast on a PTFE dish (100 mm diameter) gave robust $180 \mu\text{m}$ thick films. These demonstrate excellent mechanical properties, consistent with the polymer's high molecular mass, with a Young's modulus close to that of PIM-EA-TB and only slightly inferior to that of PIM-Trip-TB¹² (Figure S5). The mechanical properties of films of PIM-BTrip-TB make them suitable for gas permeability measurements.

Prior to gas permeability measurements, the films were soaked in methanol and dried to remove any residual traces of the casting solvent. This treatment is also known to reverse the physical aging effects of ultrapermeable glassy polymers.^{20,21} Values for gas permeabilities are shown in Table I and in Table

Table 1. Gas Permeabilities P_x , Diffusivity D_x , Solubility Coefficient S_x , and Ideal Selectivities α (P_x/P_y), α (D_x/D_y) and α (S_x/S_y) for a Methanol-Treated Film of PIM-BTrip-TB (Data from Film Aged for 166 Days in Parentheses)

	N ₂	O ₂	CO ₂	CH ₄	H ₂	He	selectivity α (P_x/P_y), α (D_x/D_y) and α (S_x/S_y) (–)			
							H ₂ /N ₂	H ₂ /CH ₄	CO ₂ /CH ₄	O ₂ /N ₂
P_x [Barrer]	926 (216)	3290 (1170)	13200 (4150)	1440 (283)	9980 (4280)	2932 (1470)	10.8 (19.8)	6.9 (15.1)	9.2 (14.7)	3.6 (5.4)
D_x [10^{-12} m ² /s]	70 (34)	347 (160)	99 (41)	28 (10)	8490 (4780)	10800 (6720)	122 (142)	306 (464)	3.55 (4.1)	5.0 (4.7)
S_x [cm ³ cm ⁻³ bar ⁻¹]	10 (4.8)	7.1 (5.5)	230 (77)	38.9 (20.6)	0.88 (0.67)	0.20 (0.16)	0.09 (0.14)	0.023 (0.033)	2.58 (3.74)	0.71 (1.14)

1 Barrer = 10^{-10} cm³ (STP) cm cm⁻² s⁻¹ cm Hg⁻¹

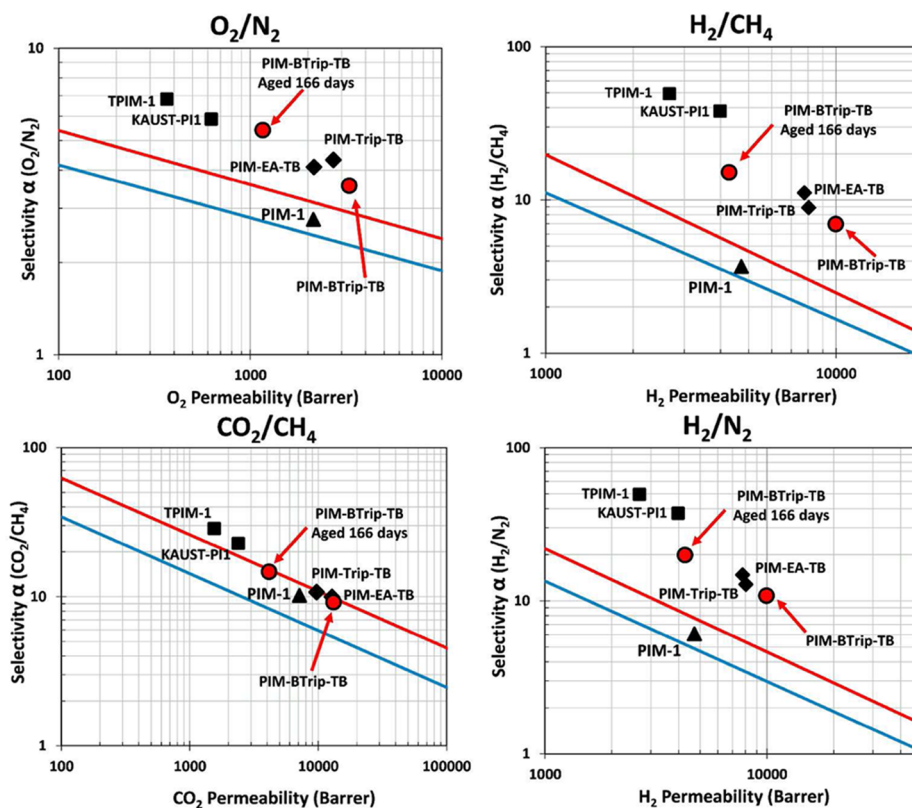


Figure 3. Robeson plots for the O₂/N₂, H₂/CH₄, CO₂/CH₄, and H₂/N₂ gas pairs showing the data for PIM-BTrip-TB both immediately after methanol treatment and after aging for 166 days. The data for PIM-1 and recently reported PIMs based on bridged bicyclic structural units are shown for comparison with their film preparation and conditioning as reported.^{10b,11a,12,14,15}

S₂, where the data are compared with those of the previously reported PIM-EA-TB and PIM-Trip-TB.^{11,12}

PIM-BTrip-TB demonstrates enhanced permeability for all gases as compared to PIM-Trip-TB, which appears consistent with the anticipated higher free volume generated by the extended triptycene unit. The order of gas permeability is CO₂ > H₂ > O₂ > CH₄ > N₂, which is the same as that for PIM-Trip-TB and most other PIMs (PIM-EA-TB differs in that H₂ is transported faster than CO₂). The exceptionally high permeabilities combined with moderate ideal selectivities place the data for PIM-BTrip-TB well above the 2008 Robeson upper bounds for the O₂/N₂, H₂/N₂, and H₂/CH₄ gas pairs and close to the upper bound for CO₂/CH₄ (Figure 3).

Physical aging is a typical feature of glassy polymers, which are in a nonequilibrium state below their T_g and undergo a relaxation process to reduce their excess free volume. This leads to a loss of permeability, usually coupled with an increase of selectivity in accordance with the Robeson trade-off.⁷ The effect

of aging is apparent for the methanol-treated film of PIM-BTrip-TB after 166 days. For example, P_{O_2} falls from 3290 to 1170 Barrer, but with an increase in selectivity from $P_{O_2}/P_{N_2} = 3.6$ to a remarkably high value of 5.4. The O₂/N₂ selectivity is especially significant owing to the similar size of the two molecules. The data point for the aged film of PIM-BTrip-TB is a similar distance above the O₂/N₂ upperbound (Figure 3) as compared to those reported by Ghanem et al. for triptycene-based PIMs, TPIM-1, and KAUST-PI-1.^{14,15}

The films used to measure gas permeabilities were thick enough for accurate determination of the gas diffusion coefficients via time lag analysis (Table 1). Due to the similar solubility coefficients for O₂ and N₂, the preferential transport of O₂ relies almost exclusively on diffusivity selectivity based on the polymer behaving as a molecular sieve. The O₂/N₂ diffusion selectivity of PIM-BTrip-TB is similar to the value that was reported for polypyrrolone-6FDA, for which the O₂/N₂ data point lies on the upper bound with an O₂/N₂ selectivity of 6.5

and an oxygen permeability of 7.5 barrer.²² However, the O₂ permeability of PIM-BTrip-TB is more than 400 times higher than for this polypyrrolone.

To conclude, a novel PIM derived from benzotriptycene and prepared using Tröger's base formation as the polymerization reaction proved highly microporous, thermally stable, and fully soluble in chloroform. Robust films were prepared by casting from solution that enabled gas permeability measurements. The results showed that PIM-BTrip-TB exceeds the overall gas permeability performance of previously reported PIM-TBs apparently due to the additional free volume generated by the benzotriptycene component. Of particular interest is the ideal selectivity for the O₂/N₂ gas pair, where exceptional oxygen permeability and reasonable selectivity demonstrate the potential of PIM-BTrip-TB as a material for polymer gas separation membranes for applications such as oxygen enrichment from air.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acsmacrolett.5b00439](https://doi.org/10.1021/acsmacrolett.5b00439).

Full experimental details for the synthesis of precursors and polymers (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: neil.mckeown@ed.ac.uk (N.B.M.).

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The research leading to these results has received funding from the European Union Seventh Framework Program (FP7/2007–2013) under grant agreement n° 608490, project M⁴CO₂.

■ REFERENCES

- (1) (a) Bernardo, P.; Drioli, E.; Golemme, G. *Ind. Eng. Chem. Res.* **2009**, *48*, 4638. (b) Baker, R. W.; Low, B. T. *Macromolecules* **2014**, *47*, 6999. (c) Xu, C.; Hedin, N. *Mater. Today* **2014**, *17*, 397. (d) Sanders, D. F.; Smith, Z. P.; Guo, R.; Robeson, L. M.; McGrath, J. E.; Paul, D. R.; Freeman, B. D. *Polymer* **2013**, *54*, 4729. (e) Zhu, X.; Tian, C.; Chai, S.; Nelson, K.; Han, K. S.; Hagaman, E. W.; Veith, G. M.; Mahurin, S. M.; Liu, H.; Dai, S. *Adv. Mater.* **2013**, *25*, 4152.
- (2) Swaidan, R.; Al-Saeedi, M.; Ghanem, B.; Litwiller, E.; Pinnau, I. *Macromolecules* **2014**, *47*, 5104.
- (3) Wang, Z.; Kathiraser, Y.; Soh, T.; Kawi, S. *J. Membr. Sci.* **2014**, *465*, 151.
- (4) (a) Gao, X.; Zou, X.; Ma, H.; Meng, S.; Zhu, G. *Adv. Mater.* **2014**, *26*, 3644. (b) Du, N.; Park, H. B.; Dal-Cin, M. M.; Guiver, M. D. *Energy Environ. Sci.* **2012**, *5*, 7306.
- (5) (a) Takasaki, Y.; Takamizawa, S. *Chem. Commun.* **2014**, *50*, 5662. (b) Mason, C. R.; Maynard-Atem, L.; Heard, K. W. J.; Satilmis, B.; Budd, P. M.; Friess, K.; Lanc, M.; Bernardo, P.; Clarizia, G.; Jansen, J. C. *Macromolecules* **2014**, *47*, 1021.
- (6) Georgis, D.; Lima, F. V.; Almansoori, A.; Daoutidis, P. *Ind. Eng. Chem. Res.* **2014**, *53*, 7461.
- (7) (a) Robeson, L. M. *J. Membr. Sci.* **1991**, *62*, 165. (b) Robeson, L. M. *J. Membr. Sci.* **2008**, *320*, 390.
- (8) Freeman, B. D. *Macromolecules* **1999**, *32*, 375.
- (9) Budd, P. M.; Ghanem, B. S.; Makhseed, S.; McKeown, N. B.; Msayib, K. J.; Tattershall, C. E. *Chem. Commun.* **2004**, 230.
- (10) (a) Budd, P. M.; McKeown, N. B.; Ghanem, B. S.; Msayib, K. J.; Fritsch, D.; Starannikova, L.; Belov, N.; Sanfirova, O.; Yampolskii, Y.; Shantarovich, V. *J. Membr. Sci.* **2008**, *325*, 851. (b) Bezzu, C. G.; Carta, M.; Tonkins, A.; Jansen, J. C.; Bernardo, P.; Bazzarelli, F.; McKeown, N. B. *Adv. Mater.* **2012**, *24*, 5930.
- (11) (a) Carta, M.; Malpass-Evans, R.; Croad, M.; Rogan, Y.; Jansen, J. C.; Bernardo, P.; Bazzarelli, F.; McKeown, N. B. *Science* **2013**, *339*, 303. (b) Carta, M.; Croad, M.; Jansen, J. C.; Bernardo, P.; Clarizia, G.; McKeown, N. B. *Polym. Chem.* **2014**, *5*, 5255. (c) Carta, M.; Malpass-Evans, R.; Croad, M.; Rogan, Y.; Lee, M.; Rose, I.; McKeown, N. B. *Polym. Chem.* **2014**, *5*, 5267.
- (12) Carta, M.; Croad, M.; Malpass-Evans, R.; Jansen, J. C.; Bernardo, P.; Clarizia, G.; Friess, K.; Lanc, M.; McKeown, N. B. *Adv. Mater.* **2014**, *26*, 3526.
- (13) Ghanem, B. S.; Hashem, M.; Harris, K. D. M.; Msayib, K. J.; Xu, M.; Budd, P. M.; Chaukura, N.; Book, D.; Tedds, S.; Walton, A.; McKeown, N. B. *Macromolecules* **2010**, *43*, 5287.
- (14) Ghanem, B. S.; Swaidan, R.; Litwiller, E.; Pinnau, I. *Adv. Mater.* **2014**, *26*, 3688.
- (15) Ghanem, B. S.; Swaidan, R.; Ma, X.; Litwiller, E.; Pinnau, I. *Adv. Mater.* **2014**, *26*, 6696.
- (16) Sydlík, S. A.; Chen, Z.; Swager, T. M. *Macromolecules* **2011**, *44*, 976.
- (17) Long, T. M.; Swager, T. M. *Adv. Mater.* **2001**, *13*, 601.
- (18) Alghunaimi, F.; Ghanem, B.; Alaslai, N.; Swaidan, R.; Litwiller, E.; Pinnau, I. *J. Membr. Sci.* **2015**, *490*, 321.
- (19) Carta, M.; Bernardo, P.; Clarizia, G.; Jansen, J. C.; McKeown, N. B. *Macromolecules* **2014**, *47*, 8320.
- (20) (a) Dai, Y.; Jian, X.; Liu, X.; Guiver, M. D. *J. Appl. Polym. Sci.* **2001**, *79*, 1685. (b) Fritsch, D.; Bengtson, G.; Carta, M.; McKeown, N. B. *Macromol. Chem. Phys.* **2011**, *212*, 1137.
- (21) (a) Huang, Y.; Paul, D. R. *Polymer* **2004**, *45*, 8377. (b) Seong, J. G.; Zhuang, Y.; Kim, S.; Do, Y. S.; Lee, W. H.; Guiver, M. D.; Lee, Y. M. *J. Membr. Sci.* **2015**, *480*, 104.
- (22) Walker, D. R. B.; Koros, W. J. *J. Membr. Sci.* **1991**, *55*, 99.