Published in final edited form as:

MRS Adv. 2018 ; 3(52): 3091–3102. doi:10.1557/adv.2018.376.

Synthesis and Characterization of Ionene-Polyamide Materials as Candidates for New Gas Separation Membranes

Jason E. Bara¹, Kathryn E. O'Harra¹, Marlow M. Durbin¹, Grayson P. Dennis¹, Enrique M. Jackson², Brian Thomas³, and Jamiu A. Odutola³

¹University of Alabama, Department of Chemical & Biological Engineering, Tuscaloosa, AL 35487-0203 USA

²NASA Marshall Space Flight Center, Huntsville, AL 35812

³Alabama A&M University, Department of Chemistry, Normal, AL 35762

Abstract

A new family of six ionenes containing aromatic amide linkages has been synthesized from readily available starting materials at scales up to ~50 g. These ionene-polyamides are all constitutional isomers and vary only in the regiochemistry of the amide linkages (para, meta) and xylyl linkages (ortho, meta, para) which are present in the polymer backbone. This paper details the synthesis of these ionenes and associated characterizations. Ionene-polyamides exhibit relatively low melting points (~150 °C) allowing them to be readily processed into films and other objects. These ionene-polyamide materials are being developed for further study as polymer membranes for the separations of gases such as CO₂, N₂, CH₄ and H₂.

Keywords

polymer; membrane; synthetic; upramolecular; organic

INTRODUCTION

Ionenes are defined as polymers that contain a ionic (typically cation) group directly within the polymer backbone.[1] Ionenes are distinctly different than ionomers which are polymers where the ionic moiety is present as a pendant to the backbone. Many commercial ionomers are anionic (e.g., salts of poly(acrylic acid) and poly(styrene sulfonic acid) although cationic ionomers are also well-known. Figure 1 presents a conceptual illustration of the differences between cationic ionenes and ionomers.

The vast majority of ionenes reported in the literature have been formed via condensation polymerizations occurring via the Menshutkin between relatively tethered 3° amines or N-heterocyclic nucleophiles (i.e., Nu-R-Nu) and dihalides (i.e., X-R'-X, where X = Cl, Br or I).[1] In many examples, the natures of the R and R' groups employed are simple alkyl, aromatic or oligo(ethylene glycol) linkages. Ionenes made in this manner typically suffer from multiple degradation mechanisms and relatively poor mechanical properties compared to conventional condensation polymers such as polyamides and polyesters. The former issue can be improved through “protecting” the cation with steric bulk and the use of less/non-

nucleophilic anions such as triflate (OTf), [2, 3] while the latter issue might be addressable through R and or R' groups containing multiple aromatic rings and/or H-bond donors and acceptors.

Given the growth in research and applications in polymerized ionic liquid (poly(IL)) ionomers, [4, 5] there is also motivation to form more sophisticated and robust ionenes which utilize functional groups from high-performance (HP) and ultra-high-performance (UHP) polymers such as polyimides and polyamides. Recently, we reported on the synthesis of a unique ionene-polyimide formed from commercially available starting materials according to Scheme 1. [6]

The first step in Scheme 1 forms a difunctional bis(imidazole) diimide monomer from 1-(3-aminopropyl)imidazole (API) and pyromellitic dianhydride (PMDA). The bis(imidazole) diimide monomer was then reacted with a stoichiometric equivalent of *p*-dichloroxylyene in the presence of lithium bistriflimide (LiTf₂N) to form the ionene-polyimide with a number average molecular weight (M_N) of ~50,000 amu. The polymer was thoroughly characterized and subsequently melt-pressed into mechanically stable thin (~90 μ m) films which were then studied as gas separation membranes for CO₂, N₂, CH₄ and H₂. The permeabilities of these gases were observed to be quite low. However, gas permeabilities of the ionene-polyimide were observed to change dramatically when films of the hybrid ionene-polyimide were soaked in an excess of [C₄mim][Tf₂N], a common ionic liquid (IL). The ionene-polyimide + IL reached an equilibrium after ~24 h where about 1 equivalent of IL was absorbed per each repeat unit of the ionene-polyimide, while no polymer appeared to dissolve into the IL. The resulting film was more flexible and exhibited gas permeabilities that had increased at least 20x for CO₂, N₂ and CH₄. Furthermore, a distinct ordering of the ionic polyimide by the IL was observed via x-ray diffractometry (XRD).

API is readily synthesized from imidazole and acrylonitrile followed by reduction with H₂ in the presence of Raney Nickel, [7] and similar species such as 1-(3-aminopropyl)-2-methylimidazole can be easily formed when starting with 2-methylimidazole or other substituted imidazole species. API-type molecules thus represent versatile building blocks for ionenes as they possess two sites of asymmetric reactivity. The primary amine is capable of forming a number of different C-N bonds while the imidazole ring acts like a tertiary amine and will remain inert unless and until an alkyl halide (or similarly reactive species) is introduced. As such, API may thus be an interesting precursor for the formation of hybrid ionene-polyamides via reaction with di(acid chlorides) such as terephthaloyl chloride (TC), isophthaloyl chloride (IC) and other aliphatic di(acid chlorides) such as adipoyl chloride.

Here, we report on the synthesis of two monomers derived from API and TC or IC which are capable of forming ionenes via the Menshutkin reaction. The compound formed from API and TC (CAS 172757-00-5) has been previously reported in the literature as a ligand for hemin (iron protoporphyrin IX), [8, 9] but was not used as a monomer for ionene synthesis. The compound formed from API and IC (CAS 349097-08-1) has not yet been reported in the literature but is offered for sale by a German fine chemical supplier. Both monomers were then reacted with *para*-, *meta*- and *ortho*-dichloroxylyene to produce ionenes and the anion was subsequently exchanged from Cl⁻ to Tf₂N⁻. The resulting ionenes were all

constitutional isomers with six different regiochemistry configurations (*p,p*, *p,m*, *p,o*, *m,p*, *m,m* and *m,o*). The ionene-polyamide products were characterized using ^1H NMR, MALDI-TOF MS, DSC and FT-IR. Ionene-polyamide materials produced were very amenable to thermal processing and can be pressed into films as well as pulled/extruded. At least one ionene-polyamide appears to behave as a thermoplastic elastomer.

MONOMER & IONENE-POLYAMIDE SYNTHESIS

Materials

TC (> 99%), API (> 97%), α , α' -Dichloro-*p*-xylene (*p*-DCX) (> 98%), α , α' -Dichloro-*m*-xylene (*m*-DCX) (> 96%), and α , α' -Dichloro-*o*-xylene (*o*-DCX) (> 97%) were purchased from TCI America. IC (98%) and K_2CO_3 (98%) were purchased from BeanTown Chemical. N-methylpyrrolidone (NMP) (ACS Grade) and CH_3CN (ACS Grade) were purchased from VWR. LiTf_2N was purchased from 3M. All materials were used as obtained, without further purification.

Monomer Synthesis

Synthesis of the two difunctional bis(imidazole) diamide monomers was performed according to Scheme 2.

Synthesis of 1,4-Benzenedicarboxamide, N^1, N^4 -bis[3-(1H-imidazol-1-yl)propyl]- “TC-API”—TC (22.12 g, 108 mmol) and K_2CO_3 (66.25 g, 479 mmol) were added to a 500 mL round bottom flask equipped with a magnetic stir bar. CH_3CN (180 mL) was then added and the reaction was stirred. API (30.00 g, 240 mmol) was next added to the reaction mixture over several minutes via a syringe. The reaction was then heated at reflux ($\sim 85^\circ\text{C}$) while stirring for 24 h. The flask was removed from heat and allowed to cool to room temperature, during which time the solids settled. Some of the CH_3CN was decanted, and the remaining contents of the flask were poured into 1 L of deionized H_2O in a 2 L Erlenmeyer flask. Additional H_2O was added to the reaction flask to help removed any solids that remained on the walls and this mixture was stirred at 40°C for ~ 2 h, in order to loosen/dissolve remaining solids. The product precipitated as a white powder, which was using a frit filter and washed with an additional ~ 500 mL H_2O . The solids were collected and dried in a vacuum oven overnight at 100°C . Yield = 32.11 g (69%) as an off-white powder. ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ 8.62 (t, $J = 5.6$ Hz, 2H), 7.92 (d, $J = 3.1$ Hz, 4H), 7.66 (s, 2H), 7.23 – 7.18 (m, 2H), 6.92 – 6.88 (m, 2H), 4.03 (t, $J = 6.9$ Hz, 4H), 3.25 (q, $J = 6.5$ Hz, 4H), 1.98 (p, $J = 6.9$ Hz, 4H).

Synthesis of 1,3-Benzenedicarboxamide, N^1, N^3 -bis[3-(1H-imidazol-1-yl)propyl]- “IC-API”—IC-API was synthesized in a similar manner as TC-API using IC (33.17 g, 163 mmol) and API (45.00 g, 360 mmol). Yield = 45.86 g (66%) as an off-white powder. ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ 8.65 (t, $J = 5.5$ Hz, 2H), 8.30 (t, $J = 1.8$ Hz, 1H), 7.97 (dd, $J = 7.7, 1.8$ Hz, 2H), 7.67 (d, $J = 1.5$ Hz, 2H), 7.56 (t, $J = 7.7$ Hz, 1H), 7.21 (d, $J = 1.3$ Hz, 2H), 6.90 (d, $J = 1.2$ Hz, 2H), 4.04 (t, $J = 6.9$ Hz, 4H), 3.26 (q, $J = 6.5$ Hz, 4H), 1.98 (p, $J = 6.9$ Hz, 4H).

Ionene-Polyamide Synthesis—Synthesis of the six ionene-polyamide isomers with varying regiochemistry was performed according to Scheme 3. For all examples, the molecular weight of a repeat unit (including the two Tf_2N^- counterions) is 1020.86 amu.

Synthesis of Ionene-Polyamide TC-API-pX—TC-API (15.00g, 39.4 mmol) and *p*-DCX (6.90g, 39.4 mmol) were added to a heavy walled round-bottom-flask (Ace Glass) equipped with a magnetic stir bar. NMP (150mL) was then added and the flask sealed with a threaded PTFE cap and DuPont Kalrez® o-ring. The reaction was heated to 150 °C and while heating, all solids were observed to dissolve while stirring for 24 h. The flask was removed from heat and allowed to cool to room temperature. It was observed that the polymer product had precipitated from solution and coated the walls of the flask as well as the stir bar. The bulk of the NMP was then decanted, and deionized H_2O was added directly to the flask. The vessel was heated to 40°C while stirring to dissolve the dark brown solids which were swollen with NMP. LiTf_2N (33.97g, 118 mmol) was dissolved in 500 mL of DI water in a 1 L Erlenmeyer flask. The dissolved product from the flask was poured into the aq. LiTf_2N solution whereupon a precipitate immediately formed. The mixture was vigorously stirred with an overhead mechanical stirrer for 1 h. Over this time, the precipitate broke apart into a pale yellow, sponge-like solid. The aqueous solution was decanted off, and the solid product was collected and dried in a vacuum oven overnight at 150°C. Yield = 37.08 g (91%) as an amber-colored, glassy solid. The ^1H NMR spectrum image for TC-API-*pX* is presented in Figure 2.

Synthesis of Ionene-Polyamide TC-API-mX—TC-API-*mX* was synthesized in a similar manner as TC-API-*pX* using TC-API (12.01 g, 32 mmol), *m*-DCX (5.53 g, 32 mmol) and LiTf_2N (27.20 g, 95 mmol). Yield = 27.41 g (84%). The ^1H NMR spectrum image for TC-API-*mX* is presented in Figure 3.

Synthesis of Ionene-Polyamide TC-API-oX—TC-API-*oX* was synthesized in a similar manner as TC-API-*pX* using TC-API (15.00 g, 39 mmol), *o*-DCX (6.90 g, 39 mmol) and LiTf_2N (33.97 g, 118 mmol). Yield = 35.13 g (86%). The ^1H NMR spectrum image for TC-API-*oX* is presented in Figure 4.

Synthesis of Ionene-Polyamide IC-API-pX—IC-API-*pX* was synthesized in a similar manner as TC-API-*pX* using IC-API (12.00 g, 32 mmol), *p*-DCX (5.52 g, 32 mmol) and LiTf_2N (27.18 g, 95 mmol). Yield = 26.02 g (79%). The ^1H NMR spectrum image for IC-API-*pX* is presented in Figure 5.

Synthesis of Ionene-Polyamide IC-API-mX—IC-API-*mX* was synthesized in a similar manner as TC-API-*pX* using IC-API (15.61 g, 41 mmol), *m*-DCX (7.18 g, 41 mmol) and LiTf_2N (35.36 g, 123 mmol). Yield = 26.15 g (61%). The ^1H NMR spectrum image for IC-API-*mX* is presented in Figure 6.

Synthesis of Ionene-Polyamide IC-API-oX—IC-API-*oX* was synthesized in a similar manner as TC-API-*pX* using IC-API (22.00 g, 58 mmol), *o*-DCX (10.12 g, 58 mmol) and LiTf_2N (49.82 g, 173 mmol). Yield = 42.27 g (71%). The ^1H NMR spectrum image for IC-API-*oX* is presented in Figure 7

All ^1H NMR spectra (Figures 2–7) in $\text{DMSO-}d_6$ confirm ionene formation as evidenced by the presence of the peak at ~ 9.3 ppm which is the imidazolium C(2)-H. All six samples also display the expected $-\text{CH}_2-$ peak at ~ 5.6 ppm which is associated with the xylene linkage to the imidazolium cation. There are only faint signals associated with unreacted endgroups (i.e., imidazole or $\text{Cl-CH}_2\text{-Ar}$) indicating high conversion of monomer to polymer, even though all of these ionene-polyamides precipitated from solution at some point during the 24 h reaction period

IONENE-POLYAMIDE CHARACTERIZATIONS

MALDI-TOF MS (Bruker Ultraflex) analysis was performed using an HPA matrix with ammonium citrate. All six ionene-polyamides exhibited very similar results with a broad peak indicating M_N of $\sim 50,000 - 60,000$ amu, indicating that the number average of repeat units (X_N) for ionene-polyamides was about 45–55. Representative examples of TC-API-*mX* and IC-API-*pX* are presented in Figure 8.

As all six ionene-polyamide materials displayed similar results via MALDI-TOF MS analysis, this may indicate that precipitation from the NMP solution during the condensation polymerization process is the factor determining/limiting M_N .

The thermal properties of the ionene-polyamide materials were also examined using DSC (TA Instruments, DSC Q20). All materials showed a very broad endotherm at ~ 150 °C which was also visually confirmed to be a melting point, followed by apparent degradation beginning at ~ 280 °C. Representative DSC scans for ionene-polyamides are shown in Figure 9 for TC-API-*oX* and IC-API-*oX*.

FT-IR spectra for the six ionene-polyamide materials were obtained using a Nicolet IS10 instrument. All ionene-polyamide materials displayed similar FT-IR spectra to those shown in Figure 10 for TC-API-*oX* and IC-API-*oX*.

THERMAL PROCESSING & MACROSCOPIC OBSERVATIONS

Ionene-polyamides are thermoplastics and we have been able to thermally process them at temperatures just above 150 °C. Figure 11 depicts a translucent amber disc of TC-API-*pX* of ~ 2 " diameter weighing several grams formed from melt-pressing the polymer particles between two Kapton® sheets.

Perhaps more interesting is that the TC-API-*pX* ionene is also an elastomer. Figure 12 illustrates a coil formed by pulling molten TC-API-*pX* around a $\frac{1}{4}$ " diameter stainless steel rod. The coil of TC-API-*pX* stretched to 120% elongation recovered to its initial length within 1–2 min.

CURRENT WORK

Our current work focuses on the formation of membranes and measuring gas permeation properties on ionic polyamide films seeking to understand the relationship between regiochemistry and membrane performance. The ability of ionene-polyamides to hold ILs

within their structures is also be of interest as a means of further modifying transport, thermal and mechanical properties. Additionally, we see opportunities to use these ionene-polyamide materials in 3-D printing applications.

ACKNOWLEDGMENTS

Support for this work provided by: National Science Foundation Chemical & Biological Separations (CBET-1605411) and NASA Marshall Space Flight Center (NNX17WA24P) is gratefully acknowledged. The authors thank Dr. Qiaoli Liang from the University of Alabama Chemistry Department for performing MALDI-TOF MS characterizations.

References

- [1]. Williams SR, Long TE, *Prog. Polym. Sci.* 34, 762–782 (2009).
- [2]. Wright AG, Holdcroft S, *ACS Macro Lett.* 3, 444–447 (2014).
- [3]. Hemp ST, Zhang M, Tamami M, Long TE, *Polym. Chem* 4, 3582–3590 (2013).
- [4]. Yuan J, Mecerreyes D, Antonietti M, *Prog. Polym. Sci* 38, 1009–1036 (2013).
- [5]. Mecerreyes D, *Prog. Polym. Sci* 36, 1629–1648 (2011).
- [6]. Mittenthal MS, Flowers BS, Bara JE, Whitley JW, Spear SK, Roveda JD, Wallace DA, Shannon MS, Holler R, Martens R, Daly DT, *Ind. Eng. Chem. Res* 56, 5055–5069 (2017).
- [7]. Schwan TJ, *J. Heterocyclic Chem.* 4, 633–634 (1967).
- [8]. Sagara T, Takeuchi S, Kumazaki K.-i., Nakashima N, *J. Electroanal. Chem.* 396, 525–533 (1995).
- [9]. Nakashima N, Tokunaga T, Owaki H, Murakami H, Sagara T, *Colloid Surface A* 169, 163–170 (2000).

Figure 1:

Illustration depicting the differences between ionomers (left) and ionenes (right).

Reprinted with permission from Mittenthal, M. S.; Flowers, B. S.; Bara, J. E.; Whitley, J. W.; Spear, S. K.; Roveda, J. D.; Wallace, D. A.; Holler, R.; Martens, R.; Daly, D. T. Ionic Polyimides: Hybrid Polymer Architectures and Composites with Ionic Liquids for Advanced Gas Separation Membranes. *Ind. Eng. Chem. Res.* 2017, 56, 5055–5069. Copyright 2017 American Chemical Society.

Figure 2:
 ^1H NMR spectrum image for TC-API-*pX*.

Figure 3:
 ^1H NMR spectrum image for TC-API-mX.

Figure 4:
 ^1H NMR spectrum image for TC-API-oX.

Figure 5:
 ^1H NMR spectrum image for IC-API-*p*X.

Figure 6:
 ^1H NMR spectrum image for IC-API-*mX*.

Figure 7:
 ^1H NMR spectrum image for IC-API-oX.

Figure 8: Representative MALDI-TOF MS results for ionene-polyamide materials showing a broad peak at $m/z = \sim 50,000 - 60,000$. Top: TC-API-*mX*. Bottom: IC-API-*pX*.

Figure 9:
DSC scans for TC-API-*oX* (top) and IC-API-*oX* (bottom).

Figure 10:
FT-IR spectra for TC-API-*o*X (left) and IC-API-*p*X (right).

Figure 11:
Melt-pressed disc of TC-API-*pX*.

Figure 12:
Photographs of coil formed from TC-API-*p*X (left) and elastic behavior under applied force (right).

Scheme 1:

Synthesis of ionene-polyimide previously reported by our group.

Scheme 2:

Synthesis of monomers from API with either TC (top) or IC (bottom).

Scheme 3:

Synthesis of the six ionene-polyamide constitutional isomers.