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Effects of Morphology on Ion Transport in Ionomers for Energy Storage

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Abstract

Polymer electrolytes are essential elements of current and next-generation energy storage applications. An important class of polymer electrolytes is ionomers, in which one of the ions is covalently bound to the polymer backbone. Ionomers are currently used in fuel cells, and show extraordinary promise as solid electrolytes in batteries for transportation and portable-power applications. Solid electrolytes are desirable for a variety of reasons. A primary one is safety: the lack of solvent leads to fewer electrochemical reactions (e.g. with the electrodes) and the absence of flammable liquids. Solvent-free electrolytes allow for less packaging (and hence higher energy density batteries) and easier manufacture. Single-ion conductors such as ionomers also have the advantage of higher efficiency (high lithium transference numbers), since the anions are bound to the polymer backbone and the current is primarily due to the cations that actively participate in the electrochemical reactions. However, to date ionomeric materials do not have sufficiently high conductivities. Ion transport mechanisms in ionomers and their relation to molecular structure are poorly understood, although it is known that ion transport is coupled to polymeric motion and to the nanoscale morphology of ionic aggregates that often self-assemble in the polymer matrix. In this project we investigate the morphology and ion dynamics in ionomer melts using *ab initio* calculations, NMR experiments, and both atomistic and coarse-grained molecular dynamics simulations. We find that the aggregate morphology depends strongly on polymer architecture, neutralizing cation, and degree of neutralization. This morphology in turn affects the counterion dynamics; we find that counterions diffuse more quickly in systems with percolated aggregates than in systems with discrete aggregates.

Acknowledgments

We thank Prof. Karen I. Winey for getting us interested in this topic initially and for a strong collaboration throughout the project. We thank Michelle Seitz, Francisco Buitrago, Ken Wagener, and John McCoy for many insightful conversations, emails, and meetings. We also thank Ralph Colby, Jim Runt, Frank van Swol, Harry Moffat, Laura Frink, and Karen Waldrup for helpful discussions.

Contents

1	Introduction	7
2	Results	10
2.1	Coarse-Grained MD Simulations	10
2.2	Atomistic MD Simulations	11
2.3	Ab initio calculations	12
2.4	NMR Experiments	13
2.5	Synthesis	15
	References	20

Figures

1	Molecular structure of a p9AA (top), p15AA (middle), and r15AA (bottom) acid copolymer.	8
2	GPC trace for P21AA Florida Sample	19
3	GPC trace for P21AA, sample DKM-01-067	19

Tables

1	Summary of GPC data taken at Sandia on various ionomers with comparison to U. Florida material. Samples run in THF and compared to PS standards.	18
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1 Introduction

Polymer electrolytes are essential elements of current and next-generation energy storage applications. An important class of polymer electrolytes is ionomers, in which one of the ions is covalently bound to the polymer backbone. Ionomers are currently used in fuel cells, and show extraordinary promise as solid electrolytes in batteries for transportation and portable-power applications. Solid electrolytes are desirable for a variety of reasons. A primary one is safety: the lack of solvent leads to fewer electrochemical reactions (e.g. with the electrodes) and the absence of flammable liquids. Solvent-free electrolytes allow for less packaging (and hence higher energy density batteries) and easier manufacture. Single-ion conductors such as ionomers also have the advantage of higher efficiency (high lithium transference numbers), since the anions are bound to the polymer backbone and the current is primarily due to the cations that actively participate in the electrochemical reactions [11].

However, to date ionomer melts do not have sufficiently high conductivities for use in practical applications. Ion transport mechanisms in ionomers and their relation to molecular structure are poorly understood, although it is known that ion transport is coupled to polymeric motion and to the nanoscale morphology of ionic aggregates that often self-assemble in the polymer matrix. The goal of this project was to develop and use a suite of multiscale models and tools to investigate the structure of ionic groups and aggregates in ionomers, and to predict their effects on ion transport. The ability to predictively model these materials will eventually enable the design and synthesis of new ionomers, which could lead to sizeable improvements in battery safety and performance essential for electrified vehicles.

Modeling charged polymeric systems is challenging due to the many important length scales involved, and particularly because the electrostatic forces are strong and long-ranged. Ionomers typically have a low dielectric constant, so in the absence of solvent there are strong electrostatic interactions among the ions and many of the ionic groups associate into ion pairs, multiplets, or nanoscale aggregates, with sizes in the range of about 1 nm. Conductivity in ionomers depends on the amount of association among the ions and the fraction of free cations, but these quantities are difficult to extract from experiment, and it is not clear what factors limit the conductivity. Here we focus on understanding the structure and morphology of the ionic aggregates, and the effect that morphology variations have on ion conduction through the ionomer.

There are several experimental signatures of ionic aggregates in melt ionomers [5]. First, the ionic aggregates act like temporary cross-links and therefore strongly affect the mechanical properties, such as viscosity and modulus. We did not focus on mechanical properties in this project. Additionally, ionomers typically show a broad x-ray scattering peak at low wavevectors known as the “ionomer peak.” This peak is due to scattering between the aggregates, and its location gives some information regarding the length scale of aggregation. The aggregates can also sometimes be seen directly by TEM imaging. The detailed molecular nature of the aggregates, however, is difficult to extract from experiment. To date, the exact shape and composition of the aggregates in any given system has been controversial. Here, we use molecular simulation to directly probe the details of the ionic aggregation.

Figure 1. Molecular structure of a p9AA (top), p15AA (middle), and r15AA (bottom) acid copolymer.

In this project we chose to focus on a set of model ionomers, a relatively newly synthesized set of precise poly(ethylene-co-acrylic acid) [P(E-AA)] copolymers. These are regular materials with carboxylic acid groups every 9, 15, or 21 carbon atoms, synthesized in the group of Ken Wagener at the University of Florida [3]. These P(E-AA) ionomers are particularly promising for modeling because they have a well-controlled architecture and a small monomeric unit, meaning fewer atoms are required in simulations. The molecular structure of three of these copolymers is shown in Fig. 1. We use the following nomenclature to denote these polymers. The names start with a ‘p’ to denote precise or an ‘r’ to denote pseudorandom spacing of the acid group along the PE backbone; next the names have a number to indicate the average number of backbone carbons per COOH group. Samples that have been neutralized with a cation are further denoted with -Y%X, where Y is the mol % neutralization determined from elemental analysis, and X is the neutralizing cation (in this project, Li^+ , Na^+ , Cs^+ , or Zn^{+2}).

Previous experimental work on these systems includes an extensive study of a set of Zn-neutralized PE-AA materials by Seitz et al. [10] This work included x-ray scattering of p9AA, p15AA, and p21AA copolymers neutralized with varying amounts of Zn. HAADF-STEM was used to image the samples, and showed that in this case the ionic aggregates are approximately spherical in shape, and distributed with liquid-like order. All the neutralized samples showed an ionomer peak, which was fit to standard models of spheres with liquid-like packing to extract the average core size of the aggregates and the distance between them. This study inspired much of the work in this project. Questions include what is the effect of changing the cation from Zn to monovalent species (Li^+ , Na^+ , Cs^+); what are the effects of spacer length between acid groups and neutralization level; is hydrogen bonding important; and how do the acid groups and counterions affect crystallinity.

In this work we used several techniques to study the PE-AA copolymers and ionomers. Coarse-

grained (CG) models were used in molecular dynamics (MD) simulations. These are useful for understanding trends and the basic physics of ionic aggregation in polymer melts. They also allowed us to simulate the systems long enough to reach the diffusive regime for counterion motion, the only technique in this project able to really look at dynamics. Complementing the CG simulations, we also performed atomistic MD simulations, using force fields available in the literature. These simulations allowed us to look in detail at the composition of the ionic aggregates and the effects of both different cations and varying degrees of neutralization. We were also able to study the acid copolymers, without any neutralizing cations, to examine the effect of hydrogen bonding on the liquid structure. At smaller length scales, *ab initio* calculations can be used to understand details of ligand binding and polarization effects. In particular, we have looked at small clusters of a range of cations with carboxylic groups.

The project also included an experimental component to complement the modeling efforts. The main component of this was a series of NMR experiments, employing ^1H , ^{13}C , and ^7Li NMR on a variety of the pAA materials. Most recently, we also performed ^{13}C and ^{31}P NMR on a series of precise acid copolymers, including precise poly(ethylene-*co*-vinylidene phosphonic acid) (pPA) copolymers recently studied by our collaborators. Finally, we synthesized additional pAA copolymers needed for further characterization and experiments.

Most of the research performed in the course of this project has either been published, or is in preparation for publication. Hence, in the Results section below, we provide the references for these publications and reproduce their abstracts. For manuscripts currently in preparation, we give a brief summary. The full work can be found in the referenced papers. The synthesis procedure for the pAA copolymers is presented in Sec. 2.5.

2 Results

2.1 Coarse-Grained MD Simulations

We performed a detailed set of MD simulations using a coarse-grained model of the ionomers. The models were designed to be similar to the PE-AA systems fully neutralized with Na^+ . We investigated two main types of architectures: ionenes, in which the anion was placed in the polymer backbone, and pendant ionomers in which the anion was placed pendant to the polymer backbone. We also considered both precise, fully random, and a “blocky” random placement of the ions in the polymer. We analyzed both equilibrium and dynamical properties of the systems. This work has been reported in three publications. We list these here along with their abstracts.

1. “Effect of Polymer Architecture and Ionic Aggregation on the Scattering Peak in Model Ionomers,” L. M. Hall, M. J. Stevens, and A. L. Frischknecht, *Phys. Rev. Lett.*, **106**, 127801 (2011) [7].

We perform molecular dynamics simulations of coarse-grained ionomer melts with two different architectures. Regularly spaced charged beads are placed either in the polymer backbone (ionenes) or pendant to it. The ionic aggregate structure is quantified as a function of the dielectric constant. The low wave vector ionomer scattering peak is present in all cases, but is significantly more intense for pendant ions, which form compact, discrete aggregates with liquidlike interaggregate order. This is in qualitative contrast to the ionenes, which form extended aggregates.

2. “Ionic aggregate structure in ionomer melts: effect of molecular architecture on aggregates and the ionomer peak,” L. M. Hall, M. E. Seitz, K. I. Winey, K. L. Oppen, K. B. Wagener, M. J. Stevens, and A. L. Frischknecht, *J. Am. Chem. Soc.* **134**, 574 (2012) [6].

We perform a comprehensive set of coarse-grained molecular dynamics simulations of ionomer melts with varying polymer architectures and compare the results to experiments in order to understand ionic aggregation on a molecular level. The model ionomers contain periodically or randomly spaced charged beads, placed either within or pendant to the polymer backbone, with the counterions treated explicitly. The ionic aggregate structure was determined as a function of the spacing of charged beads and also depends on whether the charged beads are in the polymer backbone or pendant to the backbone. The low wavevector ionomer peak in the counterion scattering is observed for all systems, and it is sharpest for ionomers with periodically spaced pendant charged beads with a large spacing between charged beads. Changing to a random or a shorter spacing moves the peak to lower wavevector. We present new experimental X-ray scattering data on Na^+ -neutralized poly(ethylene-co-acrylic acid) ionomers that show the same two trends in the ionomer peak, for similarly structured ionomers. The order within and between aggregates, and how this relates to various models used to fit the ionomer peak, is quantified and discussed.

3. “Dynamics of Model Ionomer Melts of Various Architectures”, L. M. Hall, M. J. Stevens, and A. L. Frischknecht, *Macromolecules* (2012), in press (DOI: 10.1021/ma301308n).

Ion-containing polymers have potential as single-ion conducting battery electrolyte materials.

Their conductivity is often too low for such applications due to the low dielectric polymer backbone and resulting strong aggregation of ions. We simulate coarse-grained ionomer melts (with explicit counterions) of various polymer architectures to understand the effect of polymer connectivity on the dynamics. We report on the polymer and counterion dynamics as a function of periodically or randomly spaced charged groups, which can be placed in the backbone or pendant to it. The spacer length is also varied. The simulations reveal the mechanism of ion transport, the coupling between counterion and polymer dynamics and the dependence of the ion dynamics on polymer architecture. Within the ionic aggregates, ion dynamics is rather fluid and relatively fast. The larger scale dynamics (time and length) depends strongly on the large scale morphology of the ionomer. Systems with percolated clusters have faster counterion diffusion than systems with isolated clusters. In the systems with isolated clusters counterions diffuse through the combination, rearrangement and separation of neighboring clusters. In this process, counterions move from one cluster to another without ever being separated from a cluster. In percolated systems, the counterions can move similarly without the need for the merging of clusters. Thus, the ion diffusion does not involve a hopping process. The dynamics also depends significantly on the details of the polymer architecture beyond the aggregate morphology. Adding randomness in spacing of the charges can either increase or decrease the ion diffusion, depending on the specific type of random sequence.

2.2 Atomistic MD Simulations

To complement the coarse-grained simulations and to make more direct connections with x-ray scattering and NMR data, we performed atomistic simulations of both acid copolymers and ionomers using the all-atom OPLS force field.

1. “Atomistic simulations predict a surprising variety of morphologies in precise ionomers,” Dan S. Bolintineanu, Mark J. Stevens, and Amalie L. Frischknecht, in preparation.

The nature of ionic aggregates in ionomers remains an important open question, particularly considering its significance to their electrical and mechanical properties. We have carried out fully atomistic molecular dynamics simulations of lithium-neutralized precise ionomers that suggest the need for a novel interpretation of experimental data. In particular, we observe a rich variety of aggregate morphologies depending on neutralization level and ionic content, including string-like and percolated aggregates. This brings into question the traditional assumption of spherical ionic aggregates with liquid-like ordering that is often used to interpret experimental scattering data. We discuss additional structural features of ionic aggregates in unprecedented detail.

2. “Atomistic molecular dynamics simulations of model ionomers,” Dan S. Bolintineanu, Mark J. Stevens, and Amalie L. Frischknecht, in preparation.

Ionomers are polymers that contain a small fraction of ionic groups. Due to their unique electrical properties, ionomers are being investigated as potential solid electrolytes in mobile battery applications. However, the relationships between ionomer chemistry, morphology and ion transport are poorly understood, which has hindered the development of ionomer-based batteries. To this

end, we report atomistic molecular dynamics (MD) simulations of a model ionomer (polyethylene-co-acrylic acid) neutralized with different ions at various neutralization levels and various spacer lengths between acid groups. The structure factor computed from the simulations is in good agreement with previous experimental x-ray scattering data, which provides strong validation of the simulation methods. Our simulations provide additional insight into the shape and size of ionic clusters, which suggests the need for a novel interpretation of scattering data. In particular, we observe large networks of string-like clusters, and report quantitative features of these structures as a function of counterion type, neutralization level and spacer lengths. We quantify cation-anion and oxygen-hydrogen association, the two interactions primarily responsible for aggregate formation. We also report detailed information pertaining to local structures around cations, which is difficult to obtain experimentally and may have important consequences for ion transport properties. Overall, we show that the structural properties of ionomers are amenable to atomistic simulations, which provide a valuable complement to experimental investigations.

3. “Simulations of acid copolymers,” Christopher Lueth, Mark J. Stevens, and Amalie L. Frischknecht, in preparation.

The control of polymer architecture is crucial to obtaining desired properties. Recent advances in acyclic diene metathesis (ADMET) polymerization have led to a new family of polyethylene-based copolymers in which functional groups are precisely spaced along the polymer backbone. The acid copolymers can be further neutralized by a variety of cations to produce ionomers with precisely spaced anions. The precise spacing in these copolymers leads to more ordering in the liquid state morphology than is seen in analogous random copolymers. In the case of zinc and sodium-neutralized poly(ethylene-co-acrylic) acid ionomers, x-ray scattering indicates stronger ordering, as demonstrated by a sharp ionomer peak at low wavevectors [10, 6]. One zinc-neutralized system additionally displays long range cubic ordering of ionic aggregates [10]. A cubic ordering of aggregates has also recently been observed in a precise polyethylene copolymer with pendant phosphonic acid groups [4].

In ionomer melts, nanoscale ionic aggregates form and lead to a peak in the x-ray scattering at low wavevectors. This peak is still observable in x-ray scattering from the acid form of poly(ethylene-co-acrylic acid) (PEAA) polymers with precisely spaced acid groups [10]. A detailed understanding of the origin of this scattering is still lacking. Here, we perform atomistic molecular dynamics (MD) simulations to explore the morphology of acidic aggregates in these PEAA materials. Although they have not yet been synthesized, for comparison we also perform simulations on analogous materials with sulfonic acid functional groups instead of the acetic acid groups.

2.3 Ab initio calculations

1. “Computing the Li-7 NMR chemical shielding of hydrated Li⁺ using cluster calculations and time-averaged configurations from ab initio molecular dynamics simulations,” T. M. Alam, D. Hart and S. L. B. Rempe, *Phys. Chem. Chem. Phys.* **13**, 13629 (2011) [1].

Ab initio molecular dynamics (AIMD) simulations have been used to predict the time-averaged Li NMR chemical shielding for a Li^+ solution. These results are compared to NMR shielding calculations on smaller $\text{Li}^+(\text{H}_2\text{O})_n$ clusters optimized in either the gas phase or with a polarizable continuum model (PCM) solvent. The trends introduced by the PCM solvent are described and compared to the time-averaged chemical shielding observed in the AIMD simulations where large explicit water clusters hydrating the Li^+ are employed. Different inner- and outer-coordination sphere contributions to the Li NMR shielding are evaluated and discussed. It is demonstrated an implicit PCM solvent is not sufficient to correctly model the Li shielding, and that explicit inner hydration sphere waters are required during the NMR calculations. It is also shown that for hydrated Li^+ , the time averaged chemical shielding cannot be simply described by the population-weighted average of coordination environments containing different number of waters.

2. “Ion specific effects in carboxylate binding sites,” M. J. Stevens and S. L. B. Rempe, in preparation for *Chem. Phys. Lett.*

We present results of quantum chemistry calculation of the absolute binding free energies of carboxylate ligands to an ion: Li^+ , Na^+ , K^+ , Ca^{2+} , Cs^+ and Zn^{2+} . Li^+ is the prime candidate for use in battery electrolytes. The other ions have been part of X-ray scattering studies to understand the nature of the ionic aggregates in ionomers. The variation of ions is also used to understand the mechanism of selective ion binding and transport, or lack of it. The shortest and most computationally accessible ligand that is part of the ionomers is CH_3COO^- , the acetate ion. We have thus focused our work on the acetate molecule as a representative carboxylate ligand. We find the optimal number of ligands for the monovalent ions is two forming a bidentate structure. For the divalent ions, the optimal number is 3 forming a sixfold coordinated ion. The gas phase separation distance between the ion and the closest oxygen atoms is compared to the scattering data for ionomers. Besides determining the optimal structures, we have calculated the molecular dipole moments, which are measures of the polarisability of the molecules.

2.4 NMR Experiments

In this project, NMR experiments were performed on material obtained from the Winey group at the University of Pennsylvania, which was originally synthesized by the Wagener group at the University of Florida [3, 9]. Completed NMR characterization is described in the following three manuscripts.

1. T. M. Alam, J. E. Jenkins, M. E. Seitz, C. F. Buitrago, K. I. Winey, K. L. Opper, T. W. Baughman, and K. B. Wagener, ^1H MAS NMR Spectroscopy of Polyethylene Acrylic Acid Copolymers and Ionomers. Chapter 7 in *NMR Spectroscopy of Polymers: Innovative NMR Strategies for Complex Macromolecules*; edited by H. Cheng et al. v. 1077: American Chemical Society, 2011, p. 115-131.

High speed solid-state ^1H MAS NMR spectroscopy has been used to characterize a series of poly(ethylene-co-acrylic acid) P(E-AA) materials where the distributions of the pendant carboxylic acid group along the polymer backbone are precisely controlled. Ionomers obtained from partial

neutralization of the carboxylic acid within these P(E-AA) materials with Zn^{2+} or Li^+ were also investigated. Using a combination of 1D ^1H MAS NMR and 2D ^1H MAS NMR double quantum (DQ) and NOESY correlation experiments, details about the local P(E-AA) structure were obtained. The influence of precise versus random spacing of the carboxylic acid and the impact of Li- and Zn-neutralization on the polymer structure is discussed.

2. Janelle E. Jenkins, Michelle E. Seitz, C. Francisco Buitrago, Karen I. Winey, Kathleen L. Opper, Travis W. Baughman, Kenneth B. Wagener and Todd M. Alam, "The Impact of Zinc Neutralization on the Structure and Dynamics of Precise Polyethylene Acrylic Acid Ionomers: A Solid-State ^{13}C NMR Study," *Polymer* **53**, 3917 (2012) [8].

Solid-state ^{13}C NMR experiments were performed on a series of linear poly(ethylene-co-acrylic acid) (E-AA) copolymers with the carboxylic acid group spaced precisely or randomly along the polyethylene backbone in order to determine the impact that molar percent acid content and acid group spacing have on the structure and dynamics of these materials. The impact of Zn-neutralization is investigated in precise E-AA ionomers. ^{13}C cross-polarization (CP) NMR experiments with ^1H dipolar or ^1H spin-lock filters were utilized to identify the amorphous or crystalline components in the materials. Constraints extracted from the filtering experiments were used to fit quantitative NMR data for samples that contained both crystalline and amorphous regions. All random copolymers contained crystalline phases, while only the precise sample with the longest polyethylene run between acid groups (twenty CH_2 groups) contained a crystalline component. The crystalline phase in this precise copolymer decreased with increasing zinc content.

3. T. M. Alam, J. E. Jenkins, D. S. Bolintineanu, M. J. Stevens, A. L. Frischknecht, C. F. Buitrago, K. I. Winey, K. L. Opper, and K. B. Wagener, Heterogeneous coordination environments in lithium-neutralized ionomers identified using ^1H and ^7Li MAS NMR," *Materials* **5**, 1508 (2012) [2].

The carboxylic acid proton and the lithium coordination environments for precise and random Li-neutralized polyethylene acrylic acid P(E-AA) ionomers were explored using high speed solid-state ^1H and ^7Li MAS NMR. While the ^7Li NMR revealed only a single Li coordination environment, the chemical shift temperature variation was dependent on the precise or random nature of the P(E-AA) ionomer. The ^1H MAS NMR revealed two different carboxylic acid proton environments in these materials. By utilizing ^1H - ^7Li rotational echo double resonance (REDOR) MAS NMR experiments, it was demonstrated that the proton environments correspond to different average ^1H - ^7Li distances, with the majority of the protonated carboxylic acids having a close through space contact with the Li. Molecular dynamics simulations suggest that the shortest ^1H - ^7Li distance corresponds to un-neutralized carboxylic acids directly involved in the coordination environment of Li clusters. These solid-state NMR results show that heterogeneous structural motifs need to be included when developing descriptions of these ionomer materials.

2.5 Synthesis

Precise pE-AA copolymers were prepared in the last year of the project. These polymers have been sent to the group of Prof. Karen Winey at the University of Pennsylvania for x-ray scattering and thermal characterization, and to the group of Prof. James Runt at Pennsylvania State University for dielectric relaxation spectroscopy experiments. Details of the synthesis are reported here.

The synthesis of 1-ethoxyethyl-2-(pent-4-enyl)hept-6-enoate (1), 1-ethoxyethyl-2-(oct-7-enyl)dec-9-enoate (2), and 1-ethoxyethyl-2-(undec-10-enyl)tridec-12-enoate (3) and corresponding polymeric materials could not be reproduced following literature procedures [3]. A modified procedure is detailed below:

Representative Monomer Synthesis

2,2-di(pent-4-en-1-yl)malonic acid. In an argon-filled glove box solid NaH (7.05 g, 294 mmol) was added to a 500 mL round-bottom flask equipped with a stir bar. Anhydrous THF cooled to -35 C (150 mL) was added to form a suspension. Diethyl malonate (13.43 g, 84 mmol) was added drop-wise over the course of 10 minutes while stirring. 5-Bromo-1-pentene (25 g, 167.9 mmol) was then added drop-wise, allowed to warm to room temperature and stirred overnight. After this time, additional 5-bromo-1-pentene (5.00 g, 34 mmol) was added and the reaction mixture was vigorously refluxed for 24 hours. The mixture was then removed from the glove box, cooled in an ice bath, and water was added slowly to neutralize the remaining NaH. An additional 50 mL of water (total ~ 100 mL) and ethanol (50 mL) were added along with NaOH (16.8 g, 420 mmol) and the reaction was vigorously refluxed for 24 hours under argon. After cooling to room temperature the solution was acidified to pH ~ 2-3 with concentrated HCl and vigorously stirred for 2 - 3 hours at room temperature. The mixture was extracted with diethyl ether (10x100 mL) and chloroform (3x50 mL). The organic portions were combined and filtered through a thick pad of diatomaceous earth. The volatiles materials were removed *in vacuo* to afford an off-white residue. Addition of pentane resulted in rapid crystallization of a white solid, which was collected on a frit and washed with additional pentane to afford 2,2-di(pent-4-en-1-yl)malonic acid in 69.4 % (14.0 g, 58.3 mmol) yield. *Note:* The literature procedure details a 1-pot synthetic procedure for generation of the mono-acid. It was found that purification of intermediates was required to obtain the final product in appreciable yields. **2,2-di(oct-7-en-1-yl)malonic acid:** Starting with NaH (4.88 g, 203 mmol), diethyl malonate (9.31 g, 58.1 mmol), 8-bromo-1-octene (25 g, 131 mmol) and NaOH (5.78 g, 145 mmol) and using the above procedure the product was isolated in 58.6 % yield (11 g, 33.9 mmol). **2,2-di(undec-10-en-1-yl)malonic acid:** Starting with NaH (2.24 g, 93 mmol), diethyl malonate (4.27 g, 26.7 mmol), 11-bromoundec-1-ene (14 g, 60 mmol) and NaOH (4.73 g, 118 mmol) and using the above procedure the product was isolated in 66.3 % yield (7.04 g, 17.7 mmol).

2-(pent-4-en-1-yl)hept-6-enoic acid. 2,2-di(pent-4-en-1-yl)malonic acid (14.0 g, 58.3 mmol), decalin (50 mL), and N,N-(dimethylamino)pyridine (DMAP) (0.35 g, 2.9 mmol) were added to a 500 mL round-bottom flask equipped with a stir bar and a reflux condenser. The flask was lowered into a 190 C oil bath. The immediate release of CO₂ was evident. After the frothing had

ceased the reaction was stirred for an additional 30-45 minutes at this temperature. Decalin was then removed via distillation. Purification of the residue by flash chromatography using a hexanes:ethyl acetate gradient as the eluent gave 7.3 g of a colorless oil (37.2 mmol, 64 %). Characterization was consistent with what was reported in the literature. **2-(oct-7-enyl)dec-9-enoic acid:** Starting with 2,2-di(oct-7-en-1-yl)malonic acid (11.0 g, 33.9 mmol), decalin (50 mL), and N,N-(dimethylamino)pyridine (DMAP) (0.40 g, 3.27 mmol) and using the above procedure the product was isolated in 81.1 % yield (7.71 g, 27.5 mmol). Characterization was consistent with what was reported in the literature. **2-(undec-10-en-1-yl)tridec-12-enoic acid.** Starting with 2,2-di(undec-10-en-1-yl)malonic acid (11.0 g, 27.9 mmol), decalin (50 mL), and N,N-(dimethylamino)pyridine (DMAP) (0.34 g, 2.79 mmol) and using the above procedure the product was isolated in 71.6 % yield (7.07 g, 20.0 mmol). Characterization was consistent with what was reported in the literature.

General Procedure for Acid Protection

1-ethoxyethyl-2-(pent-4-enyl)hept-6-enoate (1). Under a flow of argon a solution of 2-(pent-4-en-1-yl)hept-6-enoic acid (7.3 g, 37.2 mmol) in diethyl ether (20 mL) was slowly added to a cooled (0 °C), degassed solution of ethyl vinyl ether (13.4 g, 186 mmol) and phosphoric acid (5-10 drops from capillary pipet) in diethyl ether (20 mL). The solution was stirred at 0 °C and slowly warmed to room temperature overnight and allowed to stir for 3 days. After this time, basic alumina (~5 g) was added and the reaction mixture stirred for 4 hours at room temperature. The mixture was filtered through a pad of alumina, which was rinsed copiously with diethyl ether. Removal of the solvent and distillation afforded the pure product as a colorless oil (5.4 g, 20.1 mmol, 54.1%) Characterization was consistent with what was reported in the literature. **1-ethoxyethyl-2-(oct-7-en-1-yl)dec-9-enoate (2).** Starting with 2-(oct-7-enyl)dec-9-enoic acid (7.9 g, 28.2 mmol), ethyl vinyl ether (10.28 g, 143 mmol) and phosphoric acid (5-10 drops from capillary pipet) the product was isolated in 83 % yield (8.3 g, 23.5 mmol). Characterization was consistent with what was reported in the literature. **1-ethoxyethyl-2-(undec-10-en-1-yl)tridec-12-enoate (3).** Starting with 2-(undec-10-enyl)tridec-12-enoic acid (5.9 g, 16.8 mmol), ethyl vinyl ether (4.87 g, 67.6 mmol) and phosphoric acid (5 drops from capillary pipet) and using the above procedure afforded a crude material. Activated charcoal was added to the crude material and the mixture stirred for one hour at room temperature. After this time, the material was filtered through a silica plug, eluted with CH₂Cl₂ and recrystallized from pentane to afford the monomer as a white solid (5.03 g, 11.52 mmol, 68.2 %). Characterization was consistent with what was reported in the literature.

General Optimized Procedure for ADMET Polymerizations.

Neat protected monomer (3 – 5 grams) was added to a 100 mL Schlenk flask equipped with a magnetic stir bar and degassed by stirring under high vacuum for 4 h at room temperature. Grubbs first-generation catalyst (100:1 monomer:catalyst) was dissolved in CH₂Cl₂ and added to the flask under argon. In the case of 1-ethoxyethyl-2-(undec-10-en-1-yl)tridec-12-enoate the solid material was dissolved in xylenes (10 mL) and the procedure carried out analogously. High vacuum was slowly applied and the mixture stirred at room temperature for 4 hours. Afterwards, the tem-

perature was slowly raised to 35 °C and the mixture stirred overnight. After this time, the solid mixture was heated to 50 °C at which point stirring resumed. Grubbs first-generation catalyst (100:1 monomer:catalyst) was dissolved in xylenes (10 mL) and added to the viscous reaction mixture. Vacuum was applied slowly and the reaction allowed to stir overnight. After this time the reaction was heated to 55 °C and Grubbs first-generation catalyst (200:1 monomer:catalyst), dissolved in xylenes (10 mL), was added to the flask and stirred under vacuum until stirring ceased. Upon cooling the room temperature, ethyl vinyl ether (~50 drops) in toluene (50 mL) was added to the flask and the mixture stirred until all solids dissolved. Precipitation of the crude solution into water (500 mL, 0.5 M HCl) afforded a brown tacky solid. The solid material was dissolved in THF and filtered through a thick pad of diatomaceous earth. The solvent was reduced and the polymer precipitated into water, collected, dried overnight in a vacuum oven and used in the next step without further purification.

Optimized Conditions for Hydrogenation.

A solution of unsaturated polymer (typically 3 – 5 grams) was dissolved in a mixture of toluene (150 mL) and 1-butanol (75 mL). Argon was bubbled through the mixture for approximately 30 minutes. Wilkinsons catalyst $[\text{RhCl}(\text{PPh}_3)_3]$ (0.5 mol %) was added to the solution, and the reactor was pressurized to 400 psi with hydrogen gas and purged three times while stirring. The reactor was then filled to 750 psi with hydrogen, and heated to 100 °C for 48 h. Upon cooling to room temperature, the solvent was removed in vacuo and the crude material was dissolved in THF and filtered through a thick pad of diatomaceous earth. Concentration of the THF and precipitation of the crude solution into water (500 mL) afforded a brown tacky solid. In the case of the P9AA and P15AA polymers, the solid material was dissolved in acetone and precipitated into a water:methanol mixture (1:1) to afford a brown tacky solid. In the case of the P21AA polymer, the residue was dissolved in THF and precipitated into methanol to afford a white solid. The polymers were dried in a vacuum oven at 65 °C overnight. Samples for GPC were prepared by sonicating a portion of the material at 30 °C in THF for a few hours prior to filtration and analysis. M_n and PDI values are relative to PS standards in THF at room temperature.

P9AA: Yield (1.95 g, 72.8 %) $M_n = 41.5 \text{ kg mol}^{-1}$, PDI = 1.9.

P15AA: Yield (1.54 g, 68.8 %) $M_n = 62.7 \text{ kg mol}^{-1}$, PDI = 1.8.

P21AA: Yield (1.20 g, 42.7 %) $M_n = 48.2 \text{ kg mol}^{-1}$, PDI = 2.4.

Note: A substantial portion of each polymer was lost as a result of optimization of the hydrogenation reaction.

A summary of the sample properties is given in Table 1. ^1H and ^{13}C NMR data were also taken for all samples (results not shown). The GPC traces for the p21AA Florida sample and our p21AA sample with $M_n = 48.2 \text{ kg/mol}$ are shown in Figs. 2 and 3, respectively; these are very similar to each other, as expected.

Ultimately, we were able to generate materials with higher molecular weights and narrower PDIs when directly compared to the materials from the Wagener group [3]. Typically for polyolefin

based materials the physical properties and mechanical strength are highly dependent on M_n . Using our synthetic procedure we were able to generate M_n in excess of 60 k, which might be of interest for further study.

Table 1. Summary of GPC data taken at Sandia on various ionomers with comparison to U. Florida material. Samples run in THF and compared to PS standards.

Polymer	Code	# Vials	Mass (g)	M_n (kg/mol)	PDI (M_w/M_n)
P21AA	Florida sample			36.0	3.06
P21AA	DKM-01-041	1	1.24	13.8	2.16
P21AA	DKM-01-067	2	1.18	48.2	2.42
P21AA	DKM-01-068	2	3.15	18.3	1.92
P15AA	DKM-01-065	4	1.54	62.7	1.78
P9AA	DKM-01-066	5	1.95	41.5	1.86
P9AA	DKM-01-071	1	2.06	27.6	1.44

Figure 2. GPC trace for P21AA Florida Sample

Figure 3. GPC trace for P21AA, sample DKM-01-067

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