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Synthesis of Precision Ionic Polyolefins Derived from Ionic Liquids

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Introduction. Herein we report the use of acyclic diene metathesis polymerization to synthesize ionic polyolefins derived from ionic liquid (IL) monomers. New imidazolium based ionomers and ionenes with perfectly regular repeat units are the result. Precision placement of the ionic group either in the polymer backbone or pendant to it generates significant variance in physical properties.

Ionomers, ionenes, and polymer gels impregnated with IL's have become the focus of intense research in the field of high performance materials and ion conductive matrices.^{1,2} Work over several decades has shown that factors such as the degree of ionic clustering, crystallinity, and other morphological characteristics play roles in the properties of these materials.^{2–5} While these features have been studied in varying degrees for *random* ionomers and well-defined ionenes, fundamental studies of the former have been limited by an inherent lack of control over the repeat unit.^{2,3,5,6}

For example, consider the complexities of partially neutralized poly(ethylene-*co*-methacrylic acid) or poly(ethylene*co*-acrylic acid) which can display up to four, often thermally contiguous, mechanical relaxations. These relaxations likely result from three contributing factors: multiple amorphous phases, a distribution of crystal thicknesses due to the statistical incorporation of comonomers, and devitrification of ionic domains.^{3,7} The situation is less complicated for amorphous ionomers, but they too contain responses from ion-depleted segments as well as devitrification of ion-rich regions.^{2,8}

Devising a reliable synthetic pathway to precision ionomers, those containing perfectly regular repeat units, allows us to fine-tune the interplay between dispersion forces which govern polymer crystallization and Coulombic attraction which regulates formation of clusters and multiplets, thus providing us the opportunity to markedly deconvolute experimental data. Ion conductivity is also of interest in ionic polymers.^{4,5,6a} Prior research from our laboratory suggests the possibility of inducing formation of channel like ion-rich regions between lamella in highly interactive precision polymers;⁹ these materials may also be valuable as unique conduction matrices.

Results and Discussion. Preparation of ADMET polymers requires that only two criteria be met: the monomer must contain an alpha-omega diene, and it, as well as any trace impurities, must not poison the catalyst. Although catalysts with varying functional group tolerances are available, the underlying theme is the exclusion of Brönsted acids or nucleophiles.¹⁰ Furthermore, the design of suitable ionomer synthons requires that either of two possible polymer synthesis routes be employed: postfunctionalization (ionization) of the polymer or polymerization of an ionic monomer. The latter path is preferred for precision polyolefin synthesis since it does not necessitate quantitative conversion in a postpolymerization modification.

Metathesis polycondensation of a fully ionic monomer carries a new challenge, in that most ionic molecules are solids with melting points well above room temperature and/ or are insoluble in organic solvents. Our approach to circumvent this problem is simply to prepare ionic monomers that are, themselves, liquids thus allowing for bulk polymerization. The imidazolium hexafluorophosphate salts are appealing as they are non-nucleophilic.

Figures 1 and 2 display the chemistry used to generate IL dienes **3** and **12** from commercially available starting materials in 88% and 16% overall isolated yields, respectively. As catalyst poisoning can be a problem, purity was thoroughly assessed. In both cases, no bromide ion was detected by the Beilstein copper-flame test after anion exchange and the final products passed elemental analysis (Anal. Calcd for **3**: C, 57.90; H, 8.75; N, 5.40. Found: C, 57.76; H, 8.79; N, 5.39. Calcd for **12**: C, 59.98; H, 9.17; N, 5.0; Found: C, 60.02; H, 9.30; N: 4.93.)

The first attempt to polymerize **3** using standard ADMET conditions (melt polymerization using Grubbs' first or second generation catalyst under high vacuum at 45 °C) yielded oligomers, apparently due to catalyst inhibition. While ethylene generation was initially observed in the form of vigorous bubbling, polymerization eventually slowed and olefin isomerization ensued regardless of whether Grubbs I or II was employed.

Ondruschka and co-workers encountered a similar situation during cross metathesis in imidazolium-based IL's, reporting that contamination by trace quantities of *N*-alkyl-imidazole was sufficient to decrease the reaction rate while simultaneously increasing catalyst death and olefin isomerization rates.¹¹ Additionally, Schanz and P'Pool observed that while ROMP with Grubbs I or II could be completely inhibited with catalytic amounts of *N*-alkyl imidazoles, full restoration of catalytic activity was achieved after addition of phosphoric acid to protonate the inhibitor.¹² Grubbs and co-workers also have found that, even in the absence of inhibitors, addition of catalytic quantities of Brönsted acids can increase the rate of catalyst initiation and turnover frequency by enhancing tricyclohexyl phosphine dissociation.¹³

At first we did not believe we were dealing with the aforementioned catalyst poisoning problem. Electrospray ionization MS, as well as ¹H and ¹³C NMR spectra for **3**, showed no evidence of *N*-alkyl-imidazole contamination, and elemental analysis agreed with the theoretical values. However, further mass spectral data collected by atmospheric pressure chemical ionization, which selectively detects semivolatile compounds, combined with HPLC MS, qualitatively indicated the presence of trace quantities of imidazole **1**. This observation led us to investigate the use of phosphoric acid as in Schanz and P'Pool's work. The concentration of acid was varied from 1 to 25 mol % with

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respect to monomer (Figure 3); olefin isomerization was effectively halted with the addition of 10 mol % acid; higher concentrations of H_3PO_4 accelerated catalyst death, as indicated by the formation of brown precipitates.

With the issues of isomerization and catalyst death addressed, driving polycondensation beyond oligomerization became a matter of enhancing removal of ethylene from the highly viscous polymerizing mass. Typically ADMET chemistry has been accomplished using magnetic agitation; however, in this case, powerful interchain interactions between ionic moieties results in a rapid viscosity increase; magnetic stirring becomes impossible even at low conversions.

We constructed a small scale high vacuum mechanical stirring apparatus capable of continuously spreading the molten polymerization matrix as a thin film, thereby maximizing the rate of ethylene removal under vacuum (see Supporting Information Figure 3). Polymerization of monomer 3 (Figure 3) proceeded rapidly using this device, generating polymer 4; 10 mol % phosphoric acid/Grubbs I led to high conversion overnight as indicated by complete conver-



Figure 1. Synthesis of ionic liquid monomer 3 for ionene preparation.

sion of terminal olefin groups to internal olefins according to ¹H NMR.

Analysis of polymer 4 by DSC and TGA reveals a T_g at -3 °C with no melting transition up to 200 °C, near the onset of thermal decomposition. Powerful interchain interactions in this precision ionene 4 preclude GPC measurements; persistent aggregation was observed in all solvents tested (hexane, toluene, diethyl ether, chloroform, THF, methylene chloride, 1,2-dichlorobenzene, acetone, DMF, DMSO, methanol, water, and DMF-LiCl solutions), as indicated by multimodality of dynamic light scattering (DLS) results. Nonetheless, NMR measurements (end groups undetectable) ensure the formation of high polymer as do its mechanical properties.

Polymerization of pendant IL monomer 12 (Figure 3) to polymer 13 was achieved using similar conditions, except that the reactor was heated to 65 °C for melt polymerization. Conversion was completed easily, as indicated by disappearance of the terminal olefin according to ¹H NMR. DSC reveals a T_g at 5 °C and a T_m at 65 °C, quite different from ionene 4. Polymer 4 is an amorphous elastomer, while polymer 13 is semicrystalline. As before, a high degree of interchain aggregation in organic solvents was observed, again precluding GPC measurements.

Dynamic mechanical analysis (DMA) data, in tensile geometry, was collected on melt pressed films, information which clearly distinguishes the mechanical differences between the in-chain material and the pendant polymer. Ionene 4 displayed the onset of a glass transition at 5 °C, consistent with the DSC result ($T_g = -3$ °C, no T_m), followed by a rubbery plateau out to 57 °C. The plateau is attributed to ionic aggregates while the second relaxation at 57 °C is believed to correspond to ion-hopping. The DMA of



Figure 2. Synthesis of ionic liquid monomer 12 for ionomer preparation.



Figure 3. Modified ADMET conditions for preparation of ionenes and ionomers from imidazolium based ionic liquids.

ionomer 13, however, did not show a sharp glass transition but rather a gradual relaxation with no clear onset, regardless of the heating rate. This broad relaxation is concomitant with what appears to be either strain-induced or cold crystallization at 50 °C, followed by liquefaction near the DSC measured melting point. (See Supporting Information Figures 1 and 2)

These new regioregular ionic polymers exhibit a high degree of interchain interaction between precisely placed ionic functionalities, an observation supported by both persistent aggregation of the polymers in a wide variety of organic solvents and their mechanical behaviors. Despite nearly equivalent ion contents, the in-chain polymer **4** is an amorphous thermoplastic elastomer, whereas the pendant polymer **13** is semicrystalline. Detailed solid-state structural and morphological analysis is underway to better understand the behavior of this new class of ionomer/ionenes, to include a systematic study of the relationship between precision ionomer/ionene structure and ion conduction.

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Supporting Information Available: Text giving experimental procedures, reactor design, and thermal characterization and figures showing DSC traces and a reactor schematic. This material is available free of charge via the Internet at http:// pubs.acs.org.

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