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Imidazolium bromide derivatives of poly(isobutylene-co-isoprene): A new class of elastomeric ionomers

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ABSTRACT

New imidazolium bromide ionomers are prepared by halide displacement from brominated poly(isobutylene-co-isoprene) (BIIR) with a variety of imidazole-based nucleophiles. N-alkylation of butylimidazole (BuIm) by the allylic halide functionality within BIIR provides stable imidazolium bromide functionality in high yields. Characterization of the resulting thermoformable ionomer by dilute solution viscosity and solid-state rheology shows the effects of ion-pair aggregation on material properties over a range of ionomer composition. Knowledge of BuIm alkylations is extended to produce thermoset ionomer derivatives through solvent-free reactions of BIIR with 1,1′(1,4-butanediyl)bis(imidazole) and imidazole, whose physical properties stem from both a covalent network and a network of ion-pair aggregates. A novel method of preparing these thermosets is described, wherein a poly(isobutylene-co-isoprene) derivative bearing pendant imidazole functionality is prepared, and heated with BIIR parent material to yield covalent crosslinks comprised of dialkylated imidazole moieties.

1. Introduction

The introduction of small amounts of ionic functionality to non-polar polymers yields ionomer derivatives that provide mechanical and adhesive properties that are superior to their parent materials [1,2]. Ionomers bearing carboxylate and sulfonate functionality have been studied extensively [3,4], but cationic ionomers have also attracted recent attention [5], owing to their activity against a range of bacteria and fungi [6] as well as their resistance to fouling by marine mollusks [7]. We are particularly interested in derivatives of isobutylene-rich elastomers, since these materials provide exceptional impermeability, oxidative stability, and vibration dampening characteristics [8]. A simple route to cationic ionomer elastomers involves nucleophilic displacement of halide from halogenated starting materials such as brominated poly(isobutylene-co-paramethylstyrene) (BIMS) and brominated poly(isobutylene-co-isoprene) (BIIR). Solvent-free reactions of these halogenated polymers with PPh_3 and tertiary amines are known to provide corresponding quaternary phosphonium [9,10] and ammonium [11,12] bromide ionomers in good yield.

This manuscript describes two advances to this ionomer chemistry – the development of a new class of imidazolium bromide ionomers, and the preparation of thermoset ionomers using single-step polymer compounding techniques. While previous research has focused on the synthesis and characterization of chemically inert ionomers, the potential to introduce ion-pairs that bear reactive functionality has been largely overlooked. Unfortunately, conventional triarylphosphines and tertiary amines are ill-suited for this application. The air-instability of most phosphines, coupled with the challenges in preparing functional phosphine nucleophiles [13], limits the practical range of P-alkylation chemistry to triphenylphosphine (PPh_3). On the other hand, tertiary amines containing reactive functional groups are available, but the vulnerability of tetraalkylammonium bromides to dealkylation is troublesome [14]. Excess amine is needed to push BIIR reactions to high conversion, and the resulting ammonium bromide salt is unstable to amine displacement by bromide or other nucleophiles [15].

This work is concerned with imidazole-derived ionomers that support a wider range of ionomer chemistry than ammonium and phosphonium analogues. A surge in the ionic liquid field has fueled interest in functional imidazoles, and has clearly demonstrated the superiour stability of their corresponding imidazolium bromide salts [16,17]. Our studies began with the synthesis and characterization of thermoformable imidazolium bromide materials produced through N-alkylation of 1-butylimidazole (BuIm) by the allylic bromide functionality within BIIR (Scheme 1). An understanding of reaction dynamics is used to prepare materials with different ion-pair contents for subsequent studies of structure-

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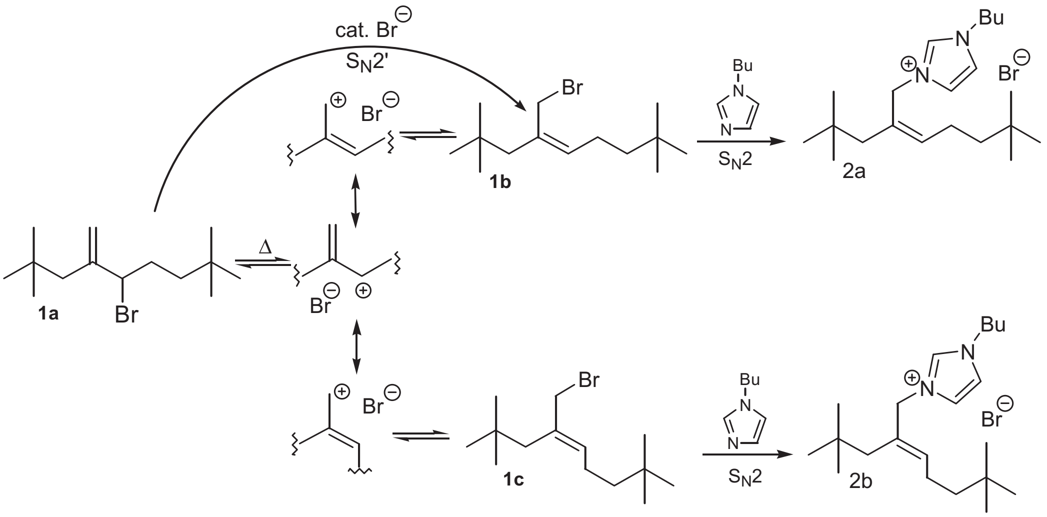

Scheme 1. N-alkylation of BuIm by **1**.

property relationships. This basic knowledge serves as a precursor to future investigations of functional ionomers, and provides a foundation for developing thermoset imidazolium ionomers.

The need for thermoset ionomer chemistry stems from the susceptibility of uncross-linked elastomeric ionomers to creep and stress relaxation [18,19]. It is well known that ion-pairs are poorly solvated by a polymer backbone of low dielectric constant, and self-assembly of ionic functionality is thermodynamically favorable [20]. The resulting aggregation of ion-pairs establishes a non-covalent network of polymer chains, whose dynamic mechanical properties approach those of conventional covalent thermosets that are comprised of carbon–carbon and/or sulfide cross-links. However, the lability of an ionic network leads to a poor response to static loads, and thermoformable ionomers do not meet the standards of engineering materials. Thermoset ionomers comprised of covalent cross-link networks and ionic functionality are required, and a direct route to their preparation is highly desirable.

The second half of this paper describes an extension of BuIm alkylation to prepare imidazolium thermosets using conventional elastomer processing methods. Products derived from solid-state reactions of BIIR + 1,1′(1,4-butanediyl)bis(imidazole) and BIIR + imidazole are characterized using model compounds before studying their cure dynamics using rheological measurements. We conclude with the preparation of an isobutylene-rich elastomer bearing pendant imidazole functionality, which is shown to provide a novel thermoset ionomer when heated with its halogenated parent material.

2. Experimental section

2.1. Materials

Brominated 2,2,4,8,8-pentamethyl-4-nonene (BPMN, **1**) was prepared as described previously [21]. The following reagents were used as received from Sigma–Aldrich (Oakville, Ontario): 1,8-bis(dimethylamino)naphthalene (Proton Sponge, 99%), 4,4′-bipyridyl (99%), 1-butylimidazole (BuIM, 98%), 1,4-dibromobutane (99%),1,4-diazabicyclo[2.2.2]octane (DABCO, 97%), ethylenebis(diphenylphosphine) (DIPHOS, 97%), 1-(2-hydroxethyl)-imidazole (97%), imidazole (99%), succinic anhydride (99%), tetrabutylammonium acetate (TBA acetate, 97%), and tricaprylmethylammonium chloride (Aliquat® 336). Brominated poly(isobutylene-co-isoprene) (BIIR or BB2030, M_w = 410 000 and polydispersity = 1.5) containing 0.15 mmol/g of allylic bromide functionality, was used as supplied by LANXESS Inc. (Sarnia, Ontario).

2.2. Synthesis of 1-n-butyl-3-[(2E,Z)-6,6-dimethyl-2-neopentylhept-2-enyl] imidazolium bromide (**2a,b**)

BPMN (0.01 mL, 0.9 g, 42.0 μmol) was heated in toluene-d_8 for 48 h at 85 °C to isomerize **1a** to a 60:40 ratio of **1b**:**1c**. The resulting solution was then charged with 1-butylimidazole (0.010 mL, 0.0095 g, 76.5 μmol) and heated for 10 h at 85 °C to give **2a,b** in quantitative yield. Solvent and residual reagents were removed by Kugelrohr distillation at 65 °C, 80 Pa. High-resolution MS analysis: required for $C_{21}H_{39}N_2^+$ *m/z* 319.3113; found *m/z* 319.3089. ^{1}H NMR ($CDCl_3$): δ 0.8–2.2 (m, 2 × $-C(CH_3)_3$, 5 × $-CH_2-$, $-CH_3$), 4.41 (t, N–**CH₂**–(CH₂)₂–CH₃), Found for Z-isomer **2a**: δ 10.67 (s, 1H, N=CH–N), 7.29 (m, 1H, NCHCHN), 7.08 (d, 1H, NCHCHN), 5.70 (t, H–C=), 4.95 (s,=C–**CH₂**–N). Found for E-isomer **2b**: δ 10.59 (s, 1H, N=CH–N), 7.30 (m, 1H, NCHCHN) 7.12 (d, 1H, NCHCHN), 5.65 (t, H–C =), 4.86 (s, = C–**CH₂**–N). 2D ROESY ^{1}H NMR was used to differentiate E and Z isomers.

2.3. Synthesis of IIR-BuImBr

BIIR (10.0 g, 1.5 mmol allylic bromide) and 1-butylimidazole (1.12 g, 9.0 mmol) were dissolved in toluene (104 mL) and heated to 100 ± 2 °C for 6 h under nitrogen. Aliquots (~0.5 mL) withdrawn at intervals were precipitated from excess acetone to isolate the polymeric reaction product, which was dried under vacuum and characterized by ^{1}H NMR spectroscopy. Samples with different imidazolium bromide contents were prepared by this method using Bu_4N acetate to quench residual electrophile at specific reaction times. For example, an IIR-BuImBr sample containing 0.05 mmol/g of imidazolium bromide was prepared by stopping N-alkylation after 3 h by adding excess Bu_4N acetate (0.678 g, 2.25 mmol) and heating for a further 2 h to convert residual allylic bromide to the corresponding acetate ester. Products were precipitated from acetone and purified by dissolution-precipitation (THF-acetone) prior to drying under vacuum.

2.4. Synthesis of 1,1′(1,4-butanediyl)bis(imidazole) (**3**)

NaOH (12.50 g) was dissolved in water (12.50 g) mixing with toluene (60 mL). Imidazole (1.31 g, 19.8 mmol) and Bu_4NBr (0.606 g, 1.98 mmol) were mixed into the solution at 25 °C until all solids