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Synthesis and characterization of thermoset imidazolium bromide ionomers

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ABSTRACT

Elastomeric ionomers are prepared via halide displacement from brominated poly(isobutylene-*co*-isoprene) (BIIR) with various imidazole-based nucleophiles. Reaction of BIIR with imidazole or 1,1′(1,4-butanediyl)bis(imidazole) in a single-step, solvent-free elastomer compounding approach is used to synthesize thermoset derivatives, in addition to a two-step process involving reaction of BIIR with 1-vinylimidazole (VIm), followed by peroxide-initiated cross-linking. The physical properties of these ionomeric thermosets are the product of their covalent and ionic networks. Ion-pair aggregation contributes significantly to dynamic storage modulus and low-strain static tensile modulus, but extensive relaxation of this labile network minimizes its influence over timescales larger than 1 min. The adhesive properties and antibacterial activity against *E. coli* provided by these ionomers are also demonstrated.

1. Introduction

The adhesion provided by the small amount of ionic functionality within ionomers makes them ideally suited for a range of polymer composite and blend applications. [1,2] Most commercial ionomers are thermoplastic materials containing carboxylate and sulfonate functionality [3,4], but materials bearing cationic functionality, including quaternary ammonium, phosphonium and imidazolium groups, have attracted recent attention [5,6], in part due to their anti-microbial activity [7,8] and their resistance to fouling by marine mollusks. [9] Unlike the small molecule ionic liquids or nanoparticle technology in present use, the polymer bound ionic functionality is not released into the environment, but retained in the thermoset indefinitely. [10,11].

Applications requiring oxidative stability and gas impermeability are well served by isobutylene-rich elastomers such as poly(isobutylene-*co*-isoprene) [12]. In addition to finding use in industrial sealants, tire inner liners [13] and pharmaceutical closures, these materials are suited to vibration dampening equipment and electrical insulating devices requiring a low dielectric constant [14]. The ionomer derivatives of present interest expand these fields of use by virtue of the influence of polymer-bound ion pairs on material properties. For example, triphenylphosphonium bromide functionality not only affects solution viscosity, [15] but enhances the dispersion of fillers such as precipitated silica and onium-ion exchanged montmorillonite clay [16].

We have recently described a series of imidazolium ionomer derivatives of brominated poly(isobutylene-*co*-isoprene), or BIIR, that can be prepared through halide displacement by imidazole-based nucleophiles. [17,18] Although early research focused on quaternary ammonium ionomers, the reversibility of N-alkylation by BIIR resulted in incomplete nucleophile conversion, yielding a thermoset containing residual amine. [19] The air-instability of most phosphines, coupled with the challenges in preparing functional phosphine nucleophiles, [20] limits practical P-alkylation chemistry to PPh_3. [21] However, imidazole-based nucleophiles offer a versatile platform for generating ionomeric elastomers, since their N-alkylation is effectively irreversible, and a wide range of functionality can be introduced through imidazole derivatization.

BIIR is effectively a random terpolymer comprised of about 98 mol% isobutylene, 1 mol% isoprene and 1 mol% allylic bromide functionality (Scheme 1). Since only the latter is reactive toward imidazole-based nucleophiles, BIIR-derived thermosets are usually depicted according to their crosslink structure, showing allylic substitution products while omitting unconverted mers for the sake of clarity. Scheme 2 provide such illustrations for the three imidazolium bromides investigated in this work.

These thermoset elastomers are produced by two distinct synthetic approaches. IIR-ImBr and IIR-BisImBr are prepared by a conventional compounding process where BIIR is mixed with the desired nucleophile to create a compound that is subsequently cross-linked in a heated compression mold. Since ionic functionality is only generated during the cure, the mixed compound has a low viscosity, making this approach

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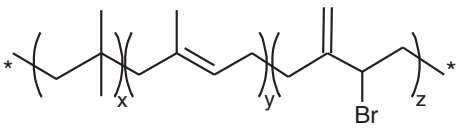
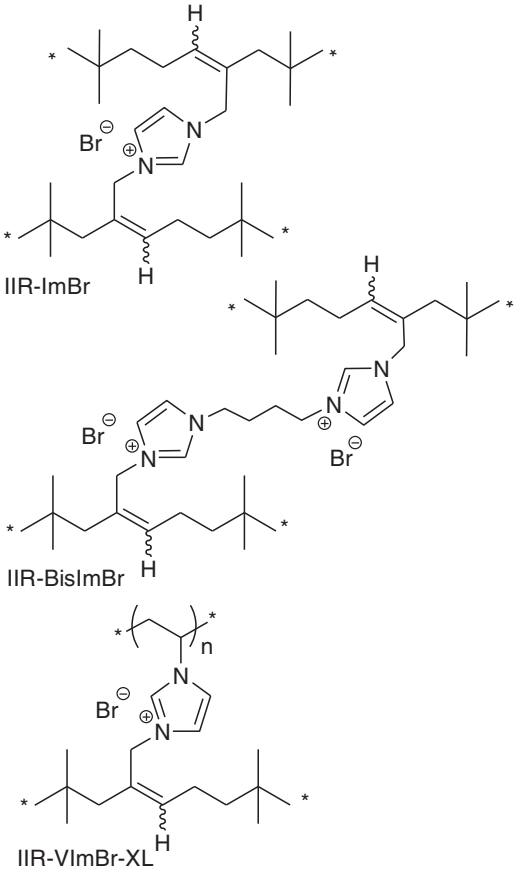


Scheme 1. Structure of BIIR.

attractive from an elastomer processing perspective. In contrast, IIR-VImBr contains imidazolium bromide bearing a peroxide-curable vinyl group. This benefits compounders of highly reinforced composites, who require heightened adhesion to assist with the incorporation and dispersion of finely divided fillers such as precipitated silica [22]. The reinforced compound can be mixed with peroxide initiator before curing in a heated compression mold to give IIR-VImBr-XL.

Although the chemical structure of these imidazolium ionomers is well characterized, the relative merits of each strategy have not been investigated, and important questions remain regarding their physical properties. Their characteristics are the product of an unusual combination of a covalent network and an ionic network. Alkylation of imidazole nucleophiles ultimately provides a covalent network that is creep resistant, while the aggregation of poorly-solvated imidazolium bromide groups gives a labile ionic network that is prone to stress relaxation. These hybrid networks have the potential to confer thermoset properties that are inaccessible using conventional, non-ionic cure technology. A complete understanding of these materials requires detailed knowledge of the covalent network density, the extent of ion pair aggregation in the solid state, and the interaction between covalent and ionic networks. This is a formidable challenge, especially since the ionic functionality within imidazolium bromide ionomers is not amenable to small angle neutron scattering analysis in the manner of alkali metal sulfonate or carboxylate systems [23].

This report details experiments that improve our knowledge of these important structure-property relationships. The synthesis of each ionomer thermoset is demonstrated at a standard reaction condition, and the contributions of their hybrid ionic/covalent networks to material properties are discussed. A brief examination of cure dynamics is followed by comparisons of tensile, adhesive and stress relaxation properties to relevant benchmark materials. We conclude with a demonstration of the anti-microbial activity that imidazolium ionomers exert against an *E. coli* bacterial culture.



Scheme 2. Cross-link functionality within imidazolium bromide thermosets.

2. Experimental

2.1. Materials

Poly (isobutylene-*co*-isoprene) (IIR, RB301) and brominated poly(isobutylene-*co*-isoprene)(BIIR, BB2030, 0.15 mmol allylic bromide functionality/g BIIR) were used as supplied by LANXESS Inc. 1-Butylimidazole (BuIm, 98%), 1-vinylimidazole (VIm, ≥99%), imidazole (≥99%), tetra-N-butylammonium bromide (Bu_4NBr, ≥98%), acrylic acid (anhydrous, 99%), 1,8-bis(dimethylamino)naphthalene (Proton Sponge©, 98%) and dicumyl peroxide (DCP, 98%) were used as received from Sigma-Aldrich. IIR-BuImBr [17], IIR-VImBr [18] IIR-Acrylate [24], 1,1′(1,4-butanediyl)bis(imidazole) [17] were prepared according to cited literature methods. Bacteriological Agar (15 g/L, Marine BioProducts) and Plate Levine EMB Agar (BD Becton Dickinson Canada) were used as received.

2.2. Compounding and physical testing

BIIR (40.0 g, 6.0 mmol allylic bromide) was mixed with 1,1′(1,4-butanediyl)bis(imidazole) (0.58 g, 3 mmol) at 90 °C and 60 rpm using a Haake Polylab R600 internal batch mixer equipped with Banbury blades. Similarly, a compound for IIR-ImBr preparation was prepared by mixing BIIR (40 g, 6.0 mmol) with 0.5 equivalents of imidazole (0.204 g, 3.0 mmol) and 0.5 equivalents of Proton Sponge (0.643 g, 3.0 mmol). IIR-VImBr (40 g) was coated with a solution of DCP (0.2 g, 0.74 mmol) in acetone (1 ml) and allowed to dry prior to mixing by passing through a 2 roll mill ten times.

Samples for tensile analysis were prepared by sheeting the desired compound (35 g) in a two-roll mill and compression-molding at 160 °C, 20 MPa for 25 min to yield a macrosheet of 2.00 ± 0.05 mm thickness. Dog bones were cut as described in ASTM D4482 [25] and analyzed at 23 ± 1 °C using an INSTRON Series 3360 universal testing instrument operating at a crosshead speed of 500 mm/min [26]. Reported results are the average of five replicate measurements.

Samples for adhesion measurements were prepared by placing sheeted compound on a Teflon sheet within the rectangular cavity of a preheated mold, and covering with a Mylar® film prior to fixing the top plate and compression molding at 20 MPa, 160 °C for 25 min. This Mylar film, made of polyethylene terephthalate, was used as a substrate from which cured elastomers were peeled, thereby providing a measure of polymer adhesion. The force required to separate a rectangular strip (25 mm wide) of cured compound from the Mylar sheet was measured at 23 ± 1 °C using a crosshead speed of 500 mm/min. Reported values are the average of 5 replicate measurements.

Samples for compression set analysis were prepared by curing the desired compound (2.5 g) in a cylindrical mold cavity (14.0 mm diameter, 12.5 mm depth) at 160 °C for 25 min. The resulting material was compressed from an initial height of 14.2 mm to a height of 6.44 mm (45% strain) for 18 h. Compression set was recorded 30 min after releasing the applied strain, with results reported as an average of four replicate experiments. This procedure was adapted from ASTM D395 – 03 (2008). [27].