

Imidazolium Ionomer Derivatives of Poly(isobutylene-co-isoprene)

By

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Abstract

The allylic bromide functionality in brominated poly(isoprene-co-isobutylene) rubber (BIIR) reacted readily to nucleophilic substitution by imidazole-derivatives. When reacted with the rubber, alkylimidazoles formed a stable non-thermoset ionomeric elastomer that has dynamic mechanical properties similar to those of vulcanizates; however, the strength is in its ion-pair aggregation. Structural characterization of the polymeric products was accomplished by spectroscopy with comparisons to the model compound prepared from brominated 2,2,4,8,8-pentamethyl-4-nonene (BPMN). Physical properties tests on the elastomers of varying ionic content (0-1 mol%) were done using solution viscosity and rheology, and demonstrated that small amounts of ionic functionality noticeably improved properties with a plateau of properties being attained as full conversion to ionic content was reached.

The reaction of imidazole with BIIR created a thermoset elastomer that formed an ionomer and thermoset after its second alkylation. These materials provided excellent scorch protection and delayed curing at high temperatures, while still reaching good storage modulus. Formation of an elastomer with a pendant imidazole group was also achieved; however, it did not perform as well as the free imidazole.

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Abbreviations

BIIR	- Brominated poly(isobutylene-co-isoprene)
BPMN	- Brominated 2,2,4,8,8-pentamethyl-4-nonene
IIR	- Poly(isobutylene-co-isoprene)
SBR	- Styrene-butadiene rubber
BR	- Polybutadiene rubber
NMR	- Nuclear magnetic resonance
SAXS	- Small angle X-ray scattering
DSC	- Differential Scanning Calorimetry
MS	- Mass Spectrometry
TBA	- Tetrabutylammonium
DCP	- Dicumyl peroxide
HVA 2	- N,N'-1,3-diphenylene-dimaleimide
BIM	- 1-Butylimidazole
BIMS	- Brominated poly(isobutylene-co-paramethylstyrene)
IM	- Imidazole

Chapter 1: Introduction

1.1 Poly(isobutylene-co-isoprene)

Poly(isobutylene-co-isoprene) (**1**), IIR, or butyl rubber is a random co-polymer that is predominately isobutylene with small amounts of isoprene units (1-3 mol%). Butyl rubber is known for its low gas permeability, good thermal and oxidative stability, as well as excellent moisture barrier and chemical resistance properties;¹ these characteristics make it suitable for the inner lining of tires. Good adhesion at lower temperatures, as well as good traction while maintaining acceptable rolling resistance, make it a highly-desired material in the manufacturing of tire treads; however, it has very poor wear- and abrasion-resistance due to limited van der Waals interaction with carbon black and other fillers, therefore, it is not used in tire treads.

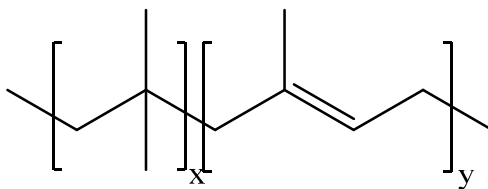


Figure 1.1: Poly(isobutylene-co-isoprene) (**1**)

IIR is synthesized by the copolymerization of 2-methylpropene (isobutylene) and 2-methyl-1,3-butadiene (isoprene) through a carbocationic polymerization that is mechanistically complex. During polymerization, isoprene adds in the trans-1,4-addition in the head-to-tail configuration¹ to the isobutylene polymer end; however, other minor

configurations such as 1,2-addition and 3,4-addition product can be noted through NMR. A low temperature is required for the polymerization of isobutylene because it decreases chain transfer, as well as keeps butyl rubber below its glass transition temperature (-68 °C). The lower the temperature is for the reaction, the greater molecular weight achieved from reduced chain transfer.²

1.2 Brominated Poly(isobutylene-co-isoprene)

Knowledge that the introduction of allylic halide functionality to butyl rubber increases its reactivity with respect to sulfur nucleophiles led to its commercial development in the 1970's.¹ IIR halogenations proceeds through an ionic pathway, wherein deprotonation of bromonium ion intermediate creates brominated poly(isobutylene-co-isoprene) (**2,3**), BIIR or bromobutyl rubber. This halogenation process makes butyl rubber suitable for tire liners, since reaction rates for bromobutyl with sulfur are comparable to that of other rubbers in the tire (natural rubber, styrene-butadiene rubber (SBR) and polybutadiene rubber (BR)). Therefore no de-lamination will occur between the different components of the tire.

As bromobutyl rubber is industrially important, there has been considerable work done to characterize its molecular structure. Bromobutyl rubber has already been characterized by NMR spectroscopy^{3,4} for "as received" bromobutyl rubber as well as other major known isomers (exomethylene, Z & E endo bromomethyl). Ho and Guthmann⁵ have demonstrated that the predominate isomer for BIIR is the kinetically-favoured

exomethylene isomer (**2**) rather than the thermodynamically-favoured E,Z-endo (bromomethyl) isomer (**3a,b**).

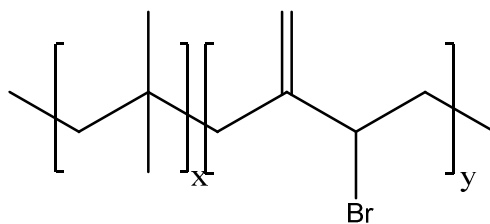


Figure 1.2: Exomethylene isomer (**2**)

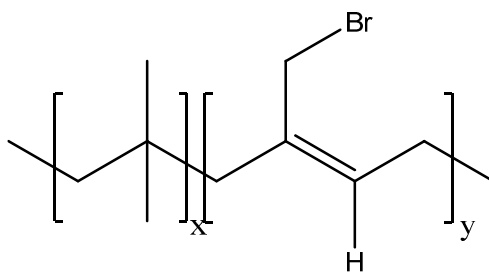


Figure 1.3: Z-Bromomethyl isomer (**3a**)

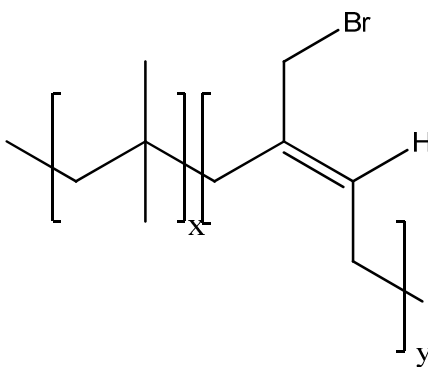
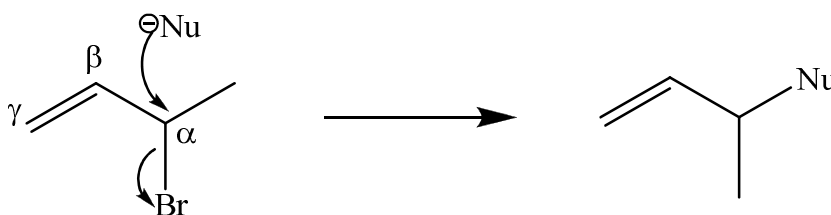


Figure 1.4: E-Bromomethyl isomer (**3b**)

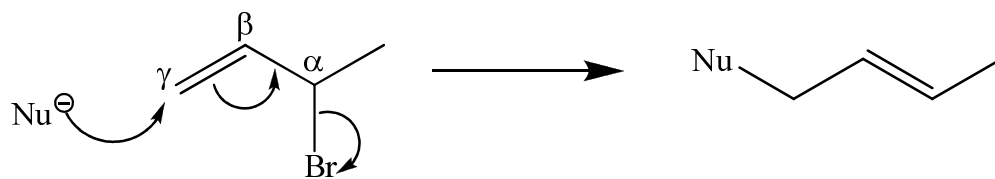
1.3 Nucleophilic Substitution of Allylic Bromide on BIIR

As discussed above, bromination of butyl rubber is required to increase the rate of reaction with sulfur during vulcanization. This development has also led to the possibility of nucleophilic substitution with the bromobutyl rubber. There are two well-known and major routes of nucleophilic substitution with allylic saturated carbons: S_N1 or unimolecular substitution, and S_N2 or bimolecular nucleophilic substitution as represented in scheme 1.1.



Scheme 1.1: S_N2 Substitution Reaction Mechanism

There is also a possibility for abnormal S_N2 : S_N2' (abnormal bimolecular nucleophilic substitution) is an extension of the normal bimolecular nucleophilic substitution as represented in scheme 1.2 as it goes through three pairs of electrons. Nucleophilic attack occurs through the sterically less hindered γ -carbon and then through the double bond to the α -carbon to displace the better leaving group, bromide.⁶ De la Mare and Vernon^{7,8} have studied allylic halogens displaced by nucleophilic displacement, and have shown that a hindered α -carbon with a double bond nearby leads to S_N2' reactions.



Scheme 1.2: S_N2' Substitution Reaction Mechanism

Scheme 1.2 is analogous to the “as received” BIIR and BPMN (the model compound brominated pentamethylnonene) where exomethylene isomer is the dominant isomer and is sterically hindered at the α -carbon, it will isomerize through S_N2' mechanism⁹ by free bromide to the more reactive endomethyl Z- and E-isomers to increase the reactivity of the BIIR.

1.4 Vulcanization of Brominated Poly(isobutylene-co-isoprene)

Vulcanization of natural rubber with sulfur has been attributed to Charles Goodyear and commercialized in 1841. Whereas uncured rubber is soft and susceptible to extensive creep, vulcanization provides a tougher material through sulfur crosslinks. When halogenated butyl rubber (and any rubber for that matter) is vulcanized it gains significant strength and the ability to hold a shape through covalent bond formation. A representation of vulcanization of rubber can be seen in Figure 1.5.

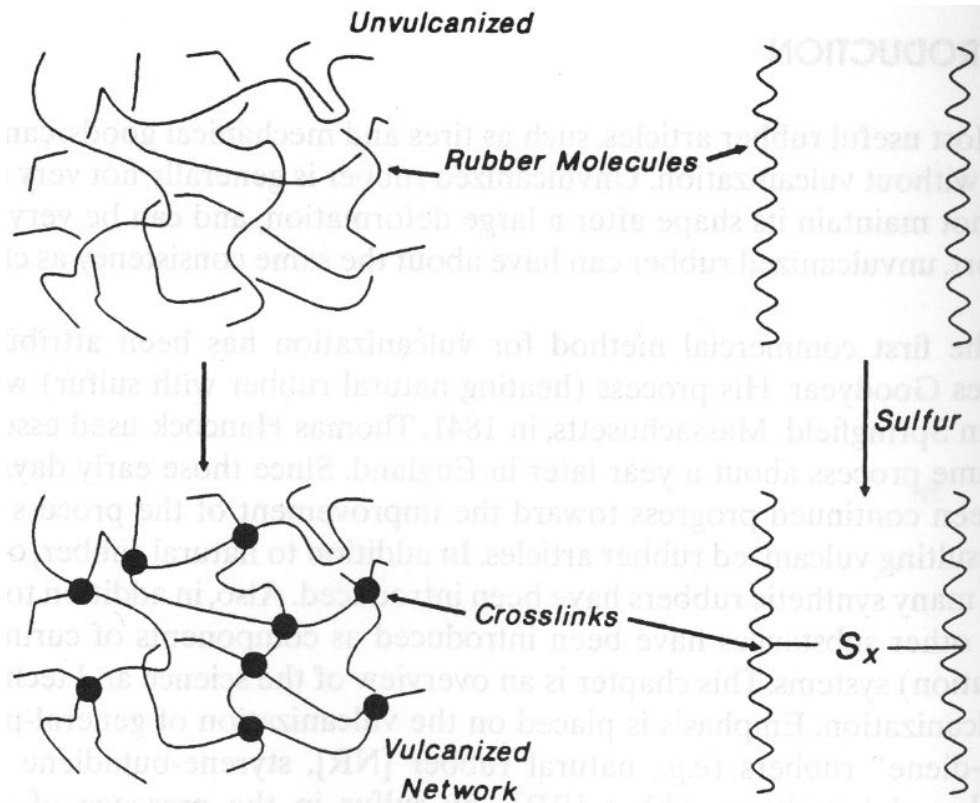


Figure 1.5: Conventional Vulcanization diagram¹⁰

Rheology is a very useful and convenient method to obtain information about the viscous and elastic response of a polymer to an applied stress. There are many different rheometers on the market but the one that was used for this research was the oscillating disc rheometer. This machine consists of two identical biconical plates which are heated and then compression mold the sample. The lower die is attached to a motor which turns in a small sinusoidal pattern while the top die is attached to a torque transducer that captures the torque and phase shift of the two signals. From the information from the machine, storage modulus (G') (how much energy was stored), loss modulus (G'') (how much energy was lost), and the complex viscosity (η^*) can be determined.

A typical representation of vulcanization cure curves can be seen in Figure 1.6. Formulations are designed to provide very little conversion at the beginning of the reaction. This time period is known as the induction period or “scorch time.” This time period, industrially, allows for the compound to take shape in the mold when there is still considerable flow in the material. The second time period is the cure period, in which the cross-links are rapidly formed and the material gains strength. The last stage is the overcure period wherein the material can revert, maintain a normal cure or have a marching cure. Cure reversion and marching cures are unstable cure, where reversion has cross-links breaking, as well as possible chain scission, both of which result in a loss of molecular weight. Marching cures increase the number of cross-link thus increasing molecular weight.

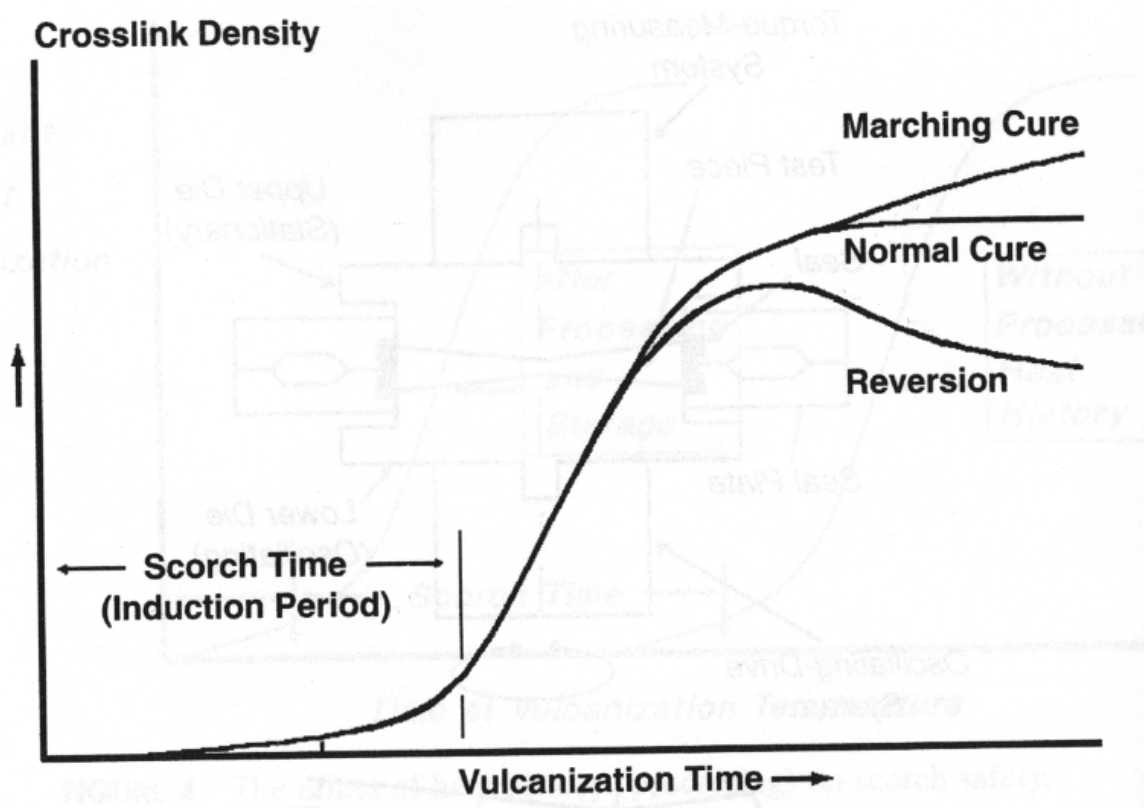


Figure 1.6: Vulcanization stages (rheometer cure curve)¹⁰

1.5 Ionomers

Ionomers are multiphase polymers that contain low levels of ionic groups (typically less than 15 mol%) along the hydrocarbon backbone.^{11,12} Although elastomeric ionomers have been around for over 40 years, they have had little commercial application or value; however, semi-crystalline ionomers can be used for adhesives, floor polish, packaging, and thin films/membranes.¹³ Small amounts of ionic functionality bound to polymers of low dielectric constant (such as BIIR) can significantly affect material properties: since the non-polar backbone cannot solvate the ionic components, there is significant ion pair

aggregation. The ions associate through multiplets of ions to create networks that have similar dynamic mechanical properties as vulcanizates.¹¹ Multiplets are aggregations of several ion pairs that have come together under ionic association in a non-polar polymer background.^{14,15} This allows fillers like carbon black to interact with the ionic groups.¹⁶ Previous work by our group demonstrated that both onium ion-exchanged montmorillonite clay and precipitated silica resulted in reduced filler agglomeration and higher degree of reinforcement¹⁷ when added to ionomer (compared to base polymer). Besides having different bond types (ionic versus covalent), the ionomers differ from vulcanizates in that they have creep problems; when large strain is induced on the ionomers, the ions hop to different multiplets causing creep,¹³ whereas covalent bonds break if sufficient strain is applied to the vulcanizates. Ionic crosslinks can be disrupted by plasticizers and elevated temperatures,¹² allowing for a reprocessibility that actually limits its applications.

There are two methods for making ionomers: copolymerization of a non-polar monomer with a low level of functional monomer, and post-polymerization modification. Post-polymerization modification is best-suited for low degrees of functionality and it is most practical for butyl rubber because butyl rubber is created through carbocationic polymerization that is incompatible with polar and/or ionic monomers.

Butyl rubber-based ionomers have been created previously using tertiary amines and triphenylphosphine.¹⁸ However, since there were issues with reversibility of ammonium

salt formation and since triphenylphosphonium bromide ionomer has only one type of functionalized group, imidazolium-based ionomers were studied.

Distinguishing ionomers from starting materials and vulcanizates can be done by rheology along with solution viscosity, differential scanning calorimetry, and small angle X-ray diffraction. Rheology can show increased storage modulus over the starting material, which suggests that the material is now tougher and stronger than before due to ionic aggregation. This could be the result of either cross-linking or of ionomer formation. To show that it is ionomer formation, solution viscosity and/or X-ray diffraction are used. Dilute solution viscosity allows for the examination of the intramolecular forces in the polymer coils. Cross-linked material will have higher viscosity than the original polymer chain since the coils will have covalent links to each other and will swell. The ionomer on the other hand will have lower viscosity because the coils are attracted to themselves (no intermolecular polymer interactions) and have a smaller hydrodynamic radius because the chains are more attracted to themselves than to the solvent. However, solution viscosity will rapidly increase as ionic content increases past the critical concentration (usually around 1 g/dL), whereas a more gradual increase occurs for non-ionomers/starting material. This method allows for lower ion content to have a noticeable effect.

Small angle X-ray scattering (SAXS) involves the shooting of a monochromatic X-ray beam through a small sample of the material. All undistorted rays are caught with a beamstop while the scattered rays are captured by a detector. The signals from the

scattering rays can then be used to determine size and shape of the nanosized particles. This can be used for ionomers as the bulk polymer does not scatter the X-rays while some types of ion pairs can. SAXS profiles can be used to spot ionic peaks in many ionomers at low angles: in particular, those with lithium counterions, heavy metals, some quaternary nitrogen, and divalent and trivalent cations.¹² SAXS is a useful technique for determining multiplet size in the polymer matrix. Unfortunately, small angle X-ray diffraction has been documented to be ineffective for previous ionomers done by the Parent group¹⁷ due to lack of contrast between the phosphonium bromide and the ammonium bromide ionomers and the background as well as very low concentration of ions.

Over time there has been a slow and steady increase in the understanding of the morphology of random ionomers, and a number of theories regarding ion structures have been proposed. The models were created to attempt to explain the information from the small-angle X-ray scattering and the physical properties (rheology and glass transition temperatures) that have been collected on several ionomers. One of the first models was the multiplet-cluster concept; multiplets were ion aggregation and clusters were heavily concentrated groups of multiplets as ionic content increased.¹⁹ However, this model only accounted for distribution of ion aggregation (SAXS) but not physical properties such as glass transition state. Similar problems have been seen with other earlier models. Core-Shell model²⁰ assumes that there is a core of ion pairs (multiplet) that is surrounded by a small section of low electron density that is covered by a region of higher electron density (less than the core) as seen in Figure 1.7 II. This concept was furthered by Roche et al.²¹

to create a lamellar structure. Both models properly modeled the SAXS; however, physical properties, such as glass transition temperatures, were not well modeled.

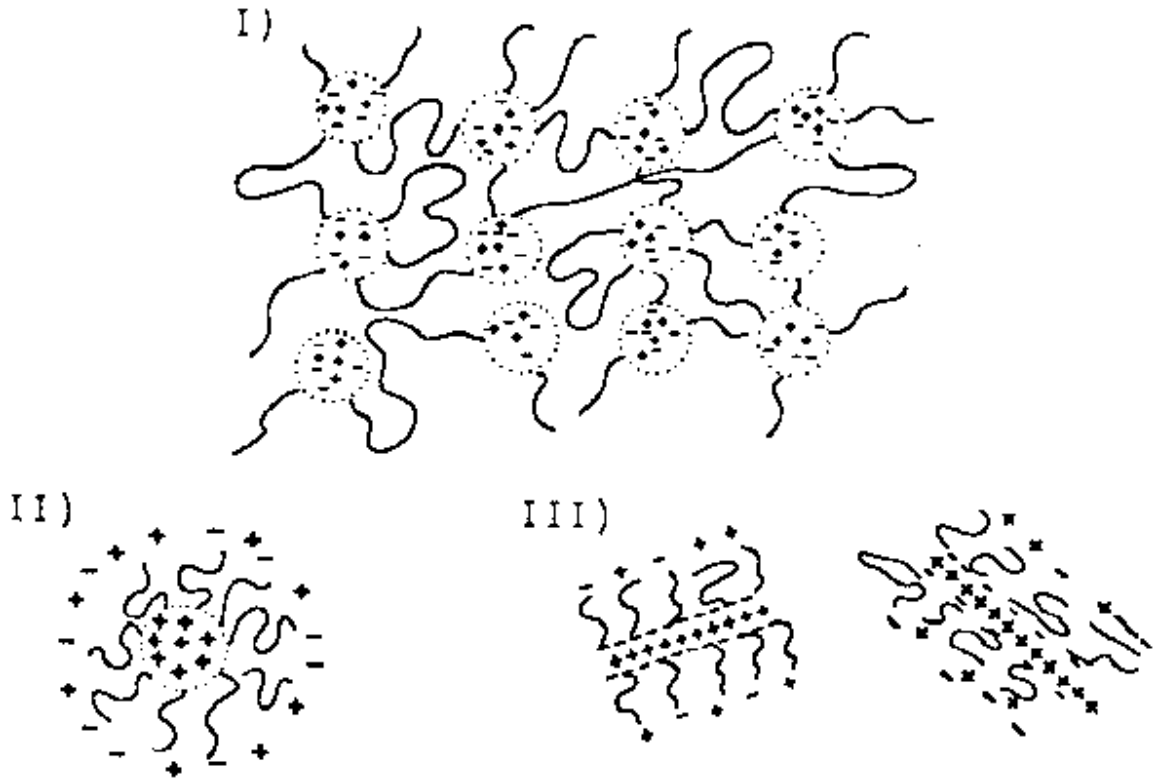


Figure 1.7: (I) Intercluster scattering model for small angle X-ray scattering from ionomers compared with (II) core-shell model and (III) lamellar intracluster models¹²

Eisenberg, Hird and Moore¹⁵ proposed the EHM model: the region directly around the ion multiplets has mobility restrictions because mobility is a function of molecular weight and the ion association gives rise to an effective increase (to the immediate area) in molecular weight. This causes a “crowding” of chains and leads to different properties than in the bulk polymer. The model postulated (Figure 1.8) on the size or thickness of the restricted region surrounding the multiplets, and although it cannot be quantified at this time, it is thought to be larger than the ion pairs. This restricted mobility region

would also have a higher glass transition temperature than the bulk polymer.¹⁵ Figure 1.8 depicts the restricted mobility region surrounding a multiplet for a poly(styrene-co-sodium methacrylate) ionomer.

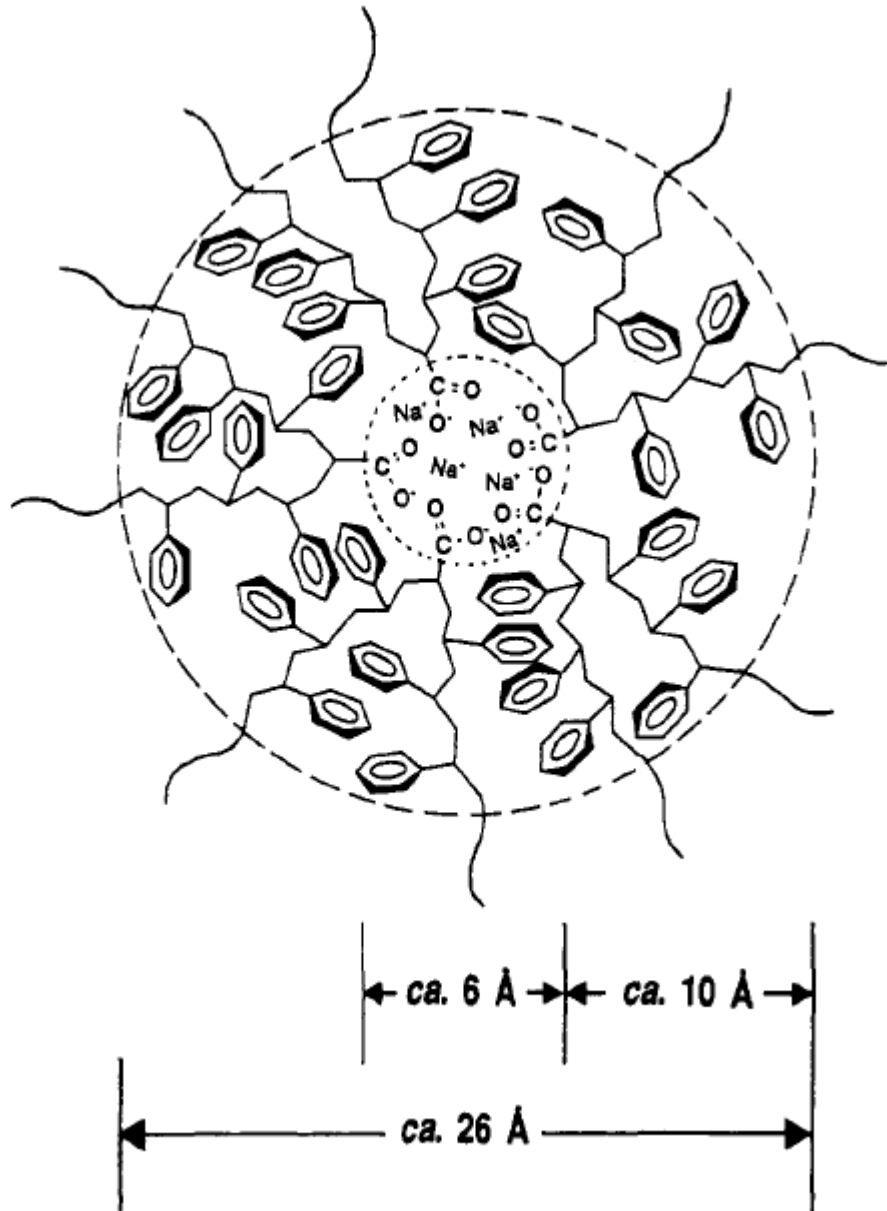


Figure 1.8: Schematic diagram of the region of restricted mobility surrounding a multiplet in a poly(styrene-co-sodium methacrylate) ionomer.¹⁵

The EHM model accounts for the SAXS results, and, it would account for the fact that ionomers are known to have two distinct glass transition temperatures (as seen through DSC). However, it has been seen that with low ion content such as BIIR ionomer-derivatives, there is only one broad glass transition temperature, as opposed to two distinct peaks because there are not enough multiplets formed and, subsequently, not enough restricted mobility regions.¹⁷ The glass transition temperature of butyl ionomers is not expected to change from the backbone polymer. Also seen by Eisenberg¹⁵ and his group was that once there is more than 4 mol% functionality, the clustered and non-clustered fractions are equal (figure 1.9 part b). At higher concentrations of ionic content, the elastomer becomes virtually all restricted mobility region leading to only one glass transition temperature. Figure 1.9 shows a good representation of low, medium and high ion content and their theoretical effect on chain mobility which is linked to glass transition temperature.

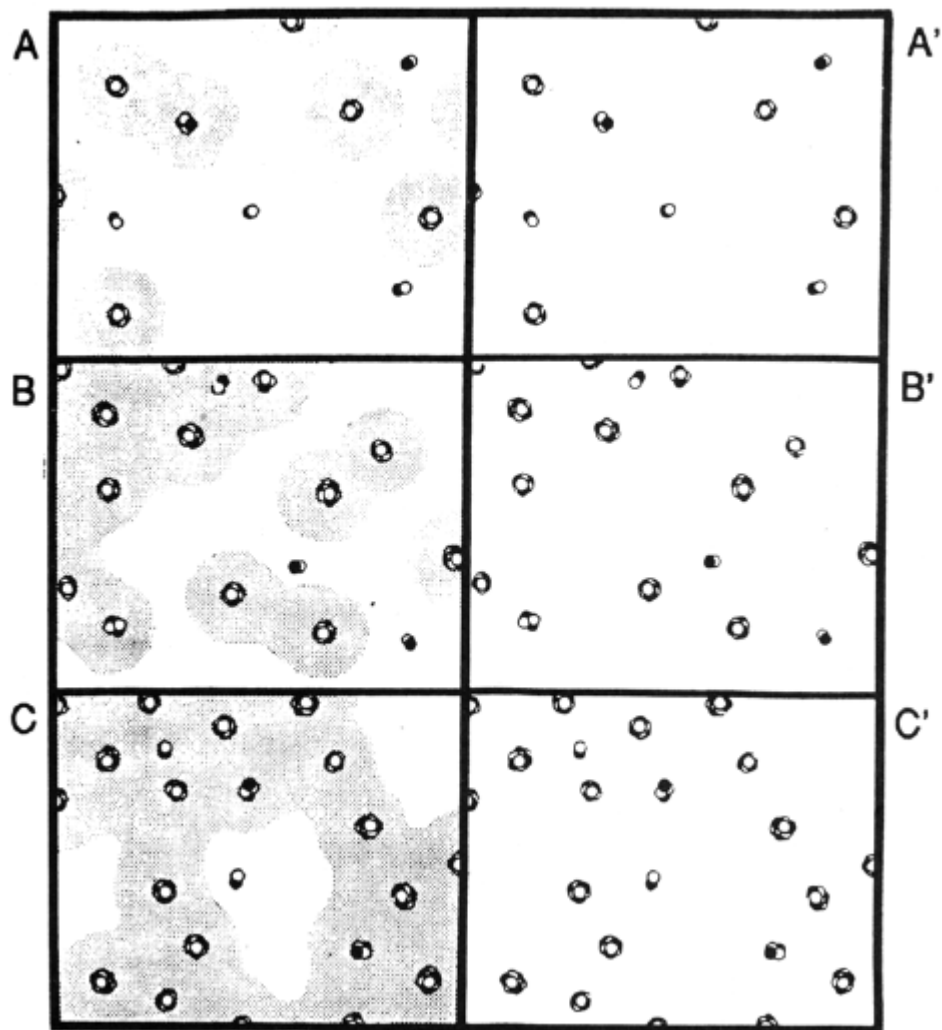


Figure 1.9: Schematic representation of the morphologies of random ionomers at different ion contents: (A) low ion content; (B) intermediate ion content; (C) high ion content. The shaded areas indicate regions of restricted mobility. A', B', and C' are schematic representations of the spatial arrangement of multiplets considering only electron density factors without regard to chain mobility¹⁵

1.6 Ionic Liquids

Ionic liquids are liquids where all of the molecules are ionic at room temperature (typically classified as ionic liquid if the ions are liquid below 100 °C)²² with a wide range of useable temperatures. They are also known to have negligible vapour pressure

due to high intermolecular interactions with good thermal stability and non-flammability. Ionic liquids have another inherent advantage over standard organic solvents as they are designer solvents (that is the cation and anion can be changed and modified for specific needs).

Early ionic liquids were 1,3-dialkylimidazolium or 1-alkylpyridinium cations with haloaluminate(III) anions ($[\text{AlCl}_4]^-$ and $[\text{Al}_2\text{Cl}_7]^-$) as the counter ions. However these ionic liquids react very vigorously with water to form hydrogen chloride gas; therefore, they must be used in a glove box with no moisture. Over time, the anions have been replaced with less water sensitive materials such as PF_6^- and halogens. Ionic liquids are a growing green technology and have been used to replace organic solvents for liquid-liquid extraction and carbon dioxide capturing, and have been used in alkylation reactions.

It has been documented that 1-methylimidazole, and by analogy 1-butylimidazole are more reactive to quaternization than oxazole, thiazole, and pyridine,²³ which makes more of a suitable nucleophile for alkylation with bromobutyl rubber.

The Parent group has shown interest in investigating the thermal stability of ionic liquids because processes in rubber modification usually go above 100 °C and sometimes reach temperatures over 200 °C if the rubber is being incorporated into a thermoplastic elastomer. Starks has seen that phosphonium ionic liquids are thermally stable to about 200 °C, whereas comparable ammonium salts are stable to just 100 °C.²⁴ Therefore

ammonium based ionomers can suffer from amine displacement by powerful nucleophiles, leading to loss of ionic functionality.¹⁸ Ngo et al.²⁵ had reported that increasing substitution on the imidazolium ion improves thermal stability, while oxygen did not have any effects on thermal decomposition. Also, it was shown that the choice of anion has a strong relationship to decomposition temperature. Hexafluorophosphate is one of the better anions for thermal stability, while halogens are the worst as they are stronger nucleophilic anions.^{25,26,27} However, imidazolium halide salts still possess thermal decomposition temperatures of around 280 °C (for 1,3-disubstituted imidazolium halide) which is much higher than the tetraalkylammonium and the phosphonium salts with halogen counter ions. This would indicate that the imidazolium bromide ionomer should be more stable than the phosphonium bromide ionomer.

1.7 Model Compound

Chu and Vukov determined that brominated 2,2,4,8,8-pentamethyl-4-nonene (BPMN) (4) was a suitable model compound for brominated poly(isobutylene-co-isoprene) for better characterization of NMR spectroscopy and Mass spectrometry.¹ Using a brominating agent rather than bromine nearly eliminates all bromine addition product from BPMN.²⁸ The model compound will be used to characterize the imidazolium-based bromide salt.

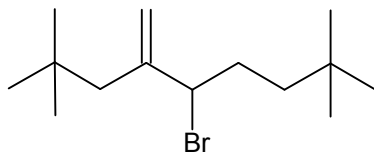


Figure 1.10: Structure of Brominated 2,2,4,8,8-Pentamethyl-4-nonene (4)

1.8 Research Objectives

The overall goal of this thesis is to prepare novel imidazolium bromide-based ionomers with butyl rubber as the backbone polymer. Specific objectives included:

1. Characterization of imidazole-based ionomers with bromobutyl rubber using spectroscopic and physical methods.
2. Investigation of thermoset ionomers using bifunctional nucleophiles with different halobutyl rubber.
3. Synthesis of non-ionomeric, non-crosslinked grafted imidazole which can be used to make a thermoset material.

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Chapter 2: Preparation of alkyimidazolium derivatives of

BIIR

2.1 Introduction

Ionomers are polymers with small amounts of ion pairs attached to the non-polar polymer backbone that aggregate to form ionic multiplets. This unique trait allows ionomers to have similar physical properties to vulcanizates.¹ The ionic aggregation is not as strong a bond as the covalent bonds of the vulcanizates; however, the ionomers are reusable as the ionic aggregation severely weakens at elevated temperatures. As previous work by the Parent group in the field of ionomers was quite successful in creating ionomers of isobutylene-based elastomers and proving the ability of heavy loading of filler material into the butyl rubber ionomer.^{2,3} The major problems with the previous ionomer systems were that they were either equilibrium-limited because of the reversibility of the N-alkylation (ammonium-based ionomer) or they lacked versatile functionality (triphenylphosphonium-based ionomer).

Since ionomers contain ion pairs that are bound to the polymer backbone, they are analogous to ionic liquids, which can be used for characterization (using model compound) and finding more possibilities for novel ionomers. There has been extensive research on ionic liquids, particularly 1,3-dialkyimidazolium derivatives, which is the focus of this chapter. As we are looking to produce a non-crosslinkable material, 1-

alkylimidazoles are a perfect place to begin and since the alkyl chain may be substituted during future work, there is more chemistry that can be done if this project is successful.

The objective for this chapter is to create an alkylimidazole ionomer with bromobutyl rubber. It is required that the ionomer is stable to exchange with other nucleophiles, and is non-crosslinking. Varying the content of the ionomer will also be studied to see its effect on the physical properties of the polymer.

2.2 Experimental Section

Materials. Brominated 2,2,4,8,8-pentamethyl-4-nonene (BPMN) was prepared as described previously.⁴ The following reagents were used as received from Sigma-Aldrich (Oakville, Ontario): tetrabutylammonium acetate (TBA acetate, 97%), 1-butyylimidazole (BIM, 98%), and dicumyl peroxide (DCP, 98%), N,N'-1,3-phenylene-dimaleimide (HVA 2, 97%), 1-decyl-2-methylimidazole (97%). Brominated poly(isobutylene-co-isoprene) (BIIR or BB2030, $M_n = 410\ 000$ and polydispersity = 1.5) containing 0.15 mmol/g of allylic bromide functionality, was used as supplied by LANXESS Inc. (Sarnia, Ontario). Brominated poly(isobutylene-co-paramethylstyrene) (BIMS or Exxpro 3745) containing 0.21 mmol/g benzylic bromide functionality was supplied by Exxon Mobil.

Solid State BIIR Reactions with BIM (5). BIIR (40 g, 6.0 mmol) was mixed with 1-butyylimidazole (BIM, 0.816 g, 6.57 mmol, 1.1 equiv with respect to allylic bromide) in a Haake Polylab R600 internal batch mixer equipped with Banbury blades and operating at

85 °C and 60 rpm. Rotation rate was reduced as needed to control temperature. Samples were taken at different reaction times in order to monitor conversion by NMR. The integration of ^1H NMR spectra of unpurified samples provided the relative concentrations for the reaction dynamics experiments (allylic CH_2 groups at δ 4.86 and 4.95 ppm).

Isomerization of BIIR from exo to endo allylic bromide microstructure. BIIR (40g, 6.0 mmol) was mixed for 120 minutes in the Haake PolyLab R600 internal batch mixer equipped with Banbury blades and operating at 115 °C and 60 rpm.

Reaction of BPMN with BIM (analogous to 5). BPMN (0.01 mL, 0.9 g, 42.0 μmol) was heated for 48 hours at 85°C in toluene- d_8 in a NMR tube to get an equilibrated ratio of E and Z-endo product. The isomerized model compound was then reacted with excess 1-butylimidazole (0.010 mL, 0.0095 g, 76.5 μmol) for 10 hours at 85°C to complete conversion to the imidazolium salt. Toluene- d_8 was removed by kugelrohr distillation for 60 minutes at 60-70 °C (P=0.6mmHg) as well as remaining reagent and the product was then dissolved in CDCl_3 (for NMR). High-resolution MS analysis required for $\text{C}_{21}\text{H}_{39}\text{N}_2^+$ m/z 319.3113; found m/z 319.3089. Final purified product analyzed by NMR. ^1H NMR (CDCl_3): δ 0.8-2.2 (m, 2 x $-\text{C}(\text{CH}_3)_3$, 3 x $-\text{CH}_2-$), 4.41 (t, N- CH_2 -(CH_2) $_2$ - CH_3). Found for E-isomer: ^1H NMR (CDCl_3): δ 4.86 (s, C- CH_2 -N), 5.65 (t, H-C=). Found for Z-isomer: ^1H NMR (CDCl_3): δ 4.95 (s, C- CH_2 -N), 5.70 (t, H-C=). 2D ROESY ^1H NMR was used to differentiate E and Z isomers.

Solution Reactions of BIIR with BIM. Toluene (104 mL), BIIR (10.0 g, 1.5 mmol), and 1-butylimidazole (1.12 g, 9.0 mmol, 6 equiv. with respect to allylic bromide) were mixed at 100 ± 2 °C for 6 hours under nitrogen atmosphere. Aliquots (~0.5 mL) were withdrawn at specific time intervals and immediately added to acetone to isolate the polymeric reaction product, which were dried under vacuum and characterized by ^1H NMR spectroscopy for reaction dynamics experiment.

Imidazolium Ionomer Stability. Tetrabutylammonium acetate (0.4532 g, 1.5 mmol, 2 equiv.) was reacted with the 1-butylimidazolium bromide ionomer (4.93g) in toluene for 3 hours at 100 °C. Polymeric reaction products were isolated by precipitation in acetone and dried under vacuum. ^1H NMR was used to characterize the product.

Variable Ionomer Content. Toluene (104 mL), BIIR (10.0 g, 1.5 mmol), and 1-butylimidazole (1.12 g, 9.0 mmol, 6 equiv. with respect to allylic bromide) were mixed at 100 ± 2 °C then reacted under nitrogen atmosphere for sufficient time to achieve required level of conversion of allylic bromide to ionomer. Excess tetrabutylammonium acetate (0.678 g, 2.25 mmol, 1.5 equiv. with respect to initial allylic bromide) was then added to the solution and allowed to react for 30 minutes (or if the total reaction time was under 5 hours, then the acetate quench was allowed to react to 5 hours) to quench any remaining allylic bromide to acetate ester. Polymeric product was isolated by precipitation in acetone then re-dissolved in tetrahydrofuran with the polymeric product re-precipitated in acetone. Polymer was then dried under vacuum. Material was milled twice and then

dried under high vacuum for 24 hours; this process was repeated and finally milled twice again. Solution viscosity and rheology experiments were then performed.

Solution Reactions of BIMS with BIM. Toluene (52 mL), BIMS (5.00 g, 1.063 mmol), and 1-butylimidazole (0.792 g, 6.38 mmol, 6 equiv. with respect to allylic bromide) were mixed at 100 ± 2 °C for 6 hours under nitrogen atmosphere. Aliquots (~0.5 mL) withdrawn at specific time intervals were immediately added to acetone to isolate the polymeric reaction product, which was dried under vacuum and then characterized by ¹H NMR spectroscopy for reaction dynamics experiment.

Solution Reactions of BIIR with 1-decyl-2methylimidazole (6). Toluene (52 mL), BIIR (5.0 g, 0.75 mmol), and 1-decyl-2-methylimidazole (1.00 g, 4.5 mmol, 6 equiv. with respect to allylic bromide) were mixed at 100 ± 2 °C for 6 hours under nitrogen atmosphere. Aliquots (~0.5 mL) withdrawn at specific time intervals were immediately added to acetone to isolate the polymeric reaction products, which were dried under vacuum and characterized by ¹H NMR spectroscopy for reaction dynamics experiment.

Peroxide cure of IIR-g-BIM. Dicumyl peroxide (0.3 wt%, 0.015g) was solution coated on IIR-g-BIM (5.0 g, 0.75 mmol) using enough acetone to dissolve the peroxide. Coated rubber was left to dry for 10 minutes to remove acetone. The rubber was mill mixed with 10 passes through the roll mill and then time cure rheology was performed.

Peroxide cure of IIR-g-BIM with HVA 2. Dicumyl peroxide (0.3 wt%, 0.015g) and N,N'-1,3-phenylene-dimaleimide (1 wt%, 0.05g) were coated on IIR-g-BIM (5.0 g, 0.75 mmol) using enough acetone to dissolve the peroxide. The coated rubber was left to dry for 10 minutes to remove acetone then mill mixed with 10 passes through the roll mill. Time cure rheology was then performed.

Analysis. NMR spectra were recorded with a Bruker Advance-600 spectrometer (600.17 MHz ^1H , 150.92 MHz ^{13}C) in deuterated chloroform (CDCl_3) with chemical shifts referenced to tetramethylsilane.

Solution viscosity for different ionomer contents was done in a series of Cannon-Fenske and Ubbelohde viscometers so that the elution time was at least 200 s (ASTM D2857-95(2001), which eliminated the need to correct for kinetic energy. Data acquired for the dilute solution region (below 1g/dL) were fitted to Huggins equation $\eta_{\text{red}} = [\eta] + k_{\text{H}}[\eta]^2c$, where η_{red} is the reduced viscosity (dL/g), $[\eta]$ is the intrinsic viscosity (dL/g), c is the polymer concentration in solution (g/dL) and k_{H} is the Huggins coefficient.⁵

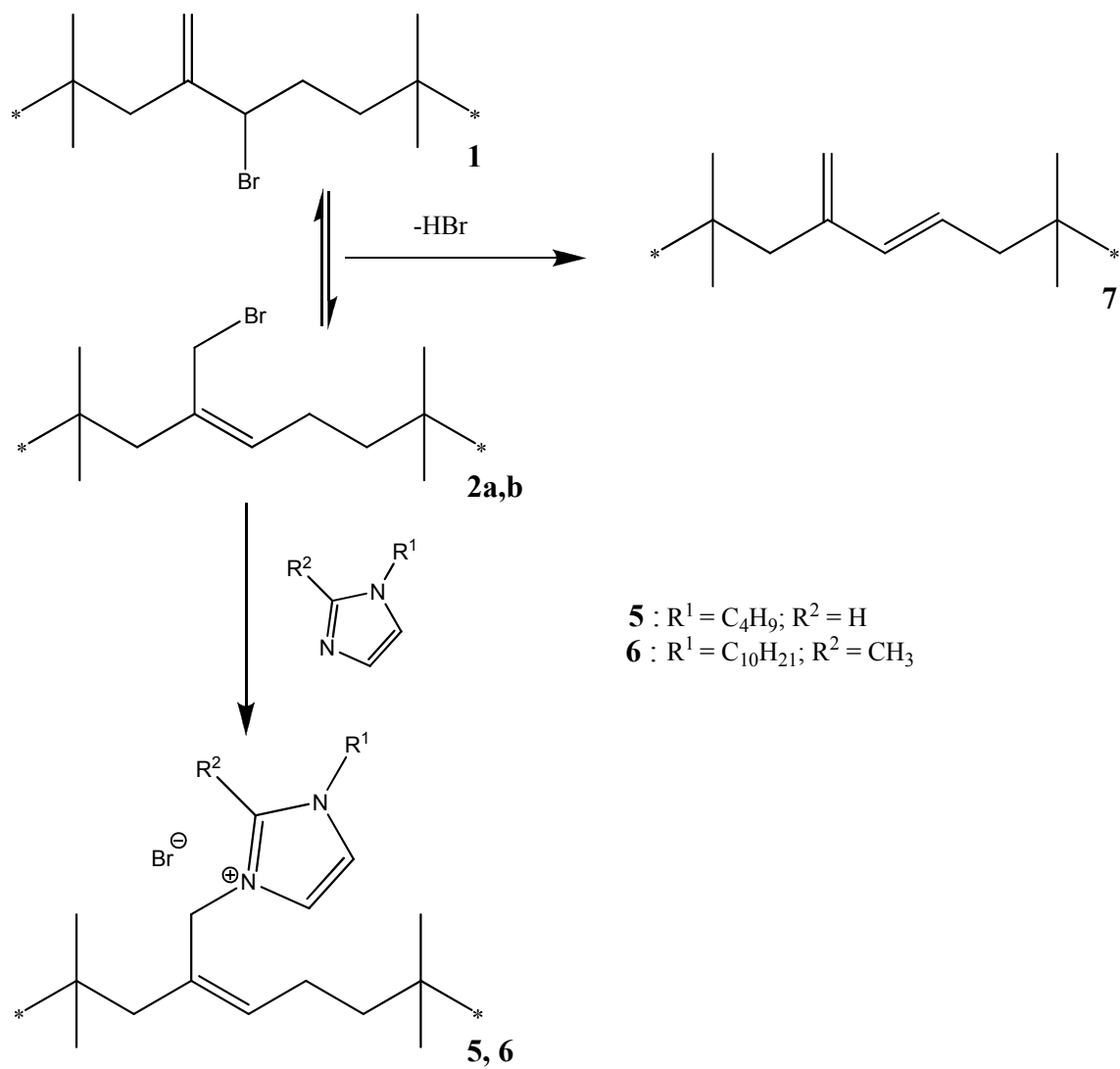
Specific masses for the model compound were identified with a Waters/Micromass GC-T TOF mass spectrometer operating in electron impact mode with high-resolution mass spectroscopy analysis.

Rheological characterization was carried out with an oscillatory rheometer (Advanced Polymer Analyzer 2000; Alpha Technologies) operating in a parallel plate configuration with a 3 degrees arc at a frequency of 1 Hz.

2.3 Results and Discussion

2.3.1 Structure and Stability of 1-Butylimidazolium Bromide ionomers

The focus of this chapter is the N-alkylation of 1-butylimidazole with BIIR to produce ion pairs of quaternary nitrogen and bromide which will form a butyl rubber-based ionomer. This reaction scheme can be seen in scheme 2.1, where “as received” (exomethylene) BIIR (**1**) isomerizes thermally over time through an S_N2' mechanism to Z,E-bromomethyl (**2a,b**). Under most conditions some HBr is produced and conjugated dienes (**7**) are formed, which reduces the amount of allylic bromide in the rubber. The isomerized rubber reacts with 1-butylimidazole to form the 1-butylimidazolium bromide product (IIR-g-BIM) (**5**). Another alkylimidazole was used for this project, 1-decyl-2-methylimidazole (**6**) which will be discussed later on. Before any physical tests can be performed, characterization of the modified polymer must be carried out. Reaction of 1-butylimidazole with the model compound (brominated 2,2,4,8,8-pentamethyl-4-nonene) (**4**) and comparison with butyl rubber ionomer by ^1H NMR can be seen in Figure 2.1. The singlet used for integration for Z-endo IIR-g-BIM can be seen at 4.96 ppm and 4.89 ppm for the E-endo IIR-g-BIM peak of interest. There is also good correlation between the peaks seen in the model compound and the bromobutyl rubber.



Scheme 2.1: N-alkylation of alkylimidazole with BIIR

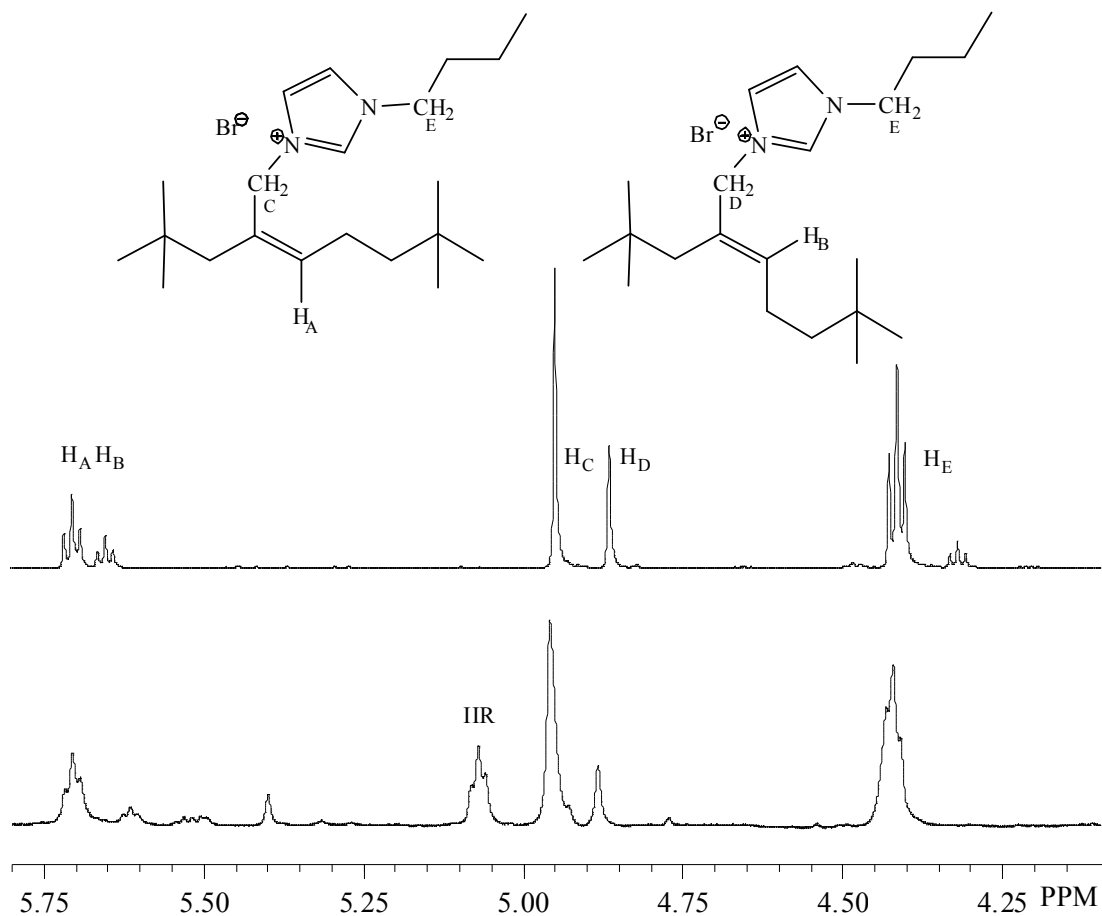


Figure 2.1: Downfield region of ^1H NMR spectra of PMN-g-BIM (top) and IIR-g-BIM (CDCl_3)

For imidazolium ionomers to be successful in commercial applications, they must be stable to exchange with stronger nucleophiles such as carboxylate. Tetrabutylammonium (TBA) acetate is known to be very reactive with isomerized bromobutyl rubber in toluene solution at elevated temperatures⁶ so it can be used to test the stability of the imidazolium product to nucleophilic exchange.

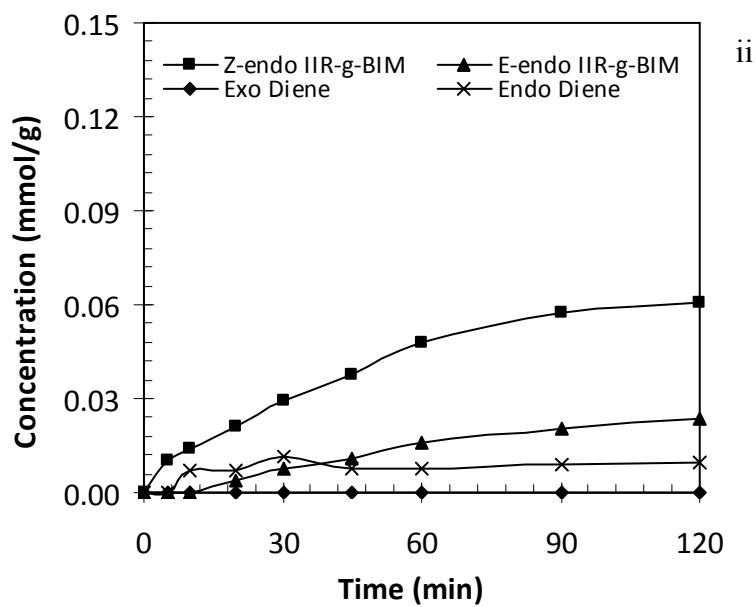
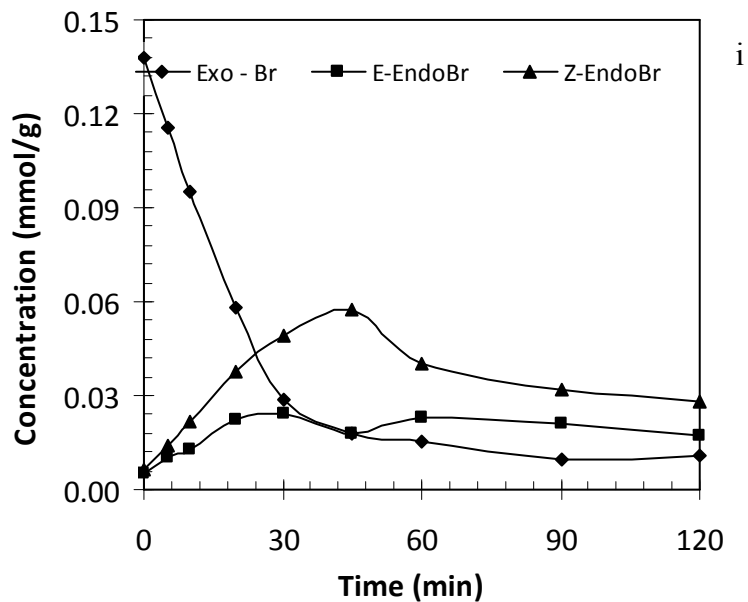
Another benefit of the TBA acetate is that it is known to be stable at elevated temperatures when reacted with bromobutyl rubber, which allows it to quench the

remaining allylic bromide for varying imidazolium ion pair content. This is important as there would not be any possibilities for other side chemistry or products being formed. A stability reaction was done for three hours at 100 °C with 1.5 equivalents of TBA acetate with IIR-g-BIM; there is no change in peaks from the start time to the conclusion of the experiment as seen in Appendix A. This proves that the imidazolium ion pairs are stable as predicted in the introduction and that TBA acetate will work well as a quench for different ionic contents.

2.3.2 Reaction Dynamics

Preparation of the butylimidazole ionomer was carried out by solid state (solvent-free) compounding at elevated temperatures. The allylic bromide content of BIIR is 0.15 mmol allylic bromide per gram of rubber, which would also be the maximum ion pair concentration. In Figure 2.2, there is moderate reaction in solid state, but, the reaction never reaches full conversion and levels off near the end of reaction time with 1.1 molar equivalents of 1-butylimidazole to allylic bromide content. It is also apparent that isomerization of exomethylene to Z- and E- endo isomers is noticeably quicker than the N-alkylation of the 1-butylimidazole. Isomerization of the rubber is not the rate determining step, and, subsequently the rubber does not need to be pre-treated, so “as received” rubber was used for the duration of the project. This is noticeably slower than both the tertiary amine and the triphenylphosphine for creating an ionomer in solid state as they reacted significantly faster with isomerization. There is considerable loss of HBr through formation of conjugate dienes (7) (a debrominated by-product) which is formed

during the reaction and which limits the amount of ion pairs available. Final conversion of allylic bromide to the alkylimidazole ion pairs was 56% for “as received” rubber and only 47% for isomerized rubber because of conjugated diene formation in the isomerization step. Since 1-butylimidazole did not alkylate quickly enough with a stoichiometric equivalent and considerable by-product was formed, a cleaner more robust solution-based reaction scheme was deemed more appropriate.



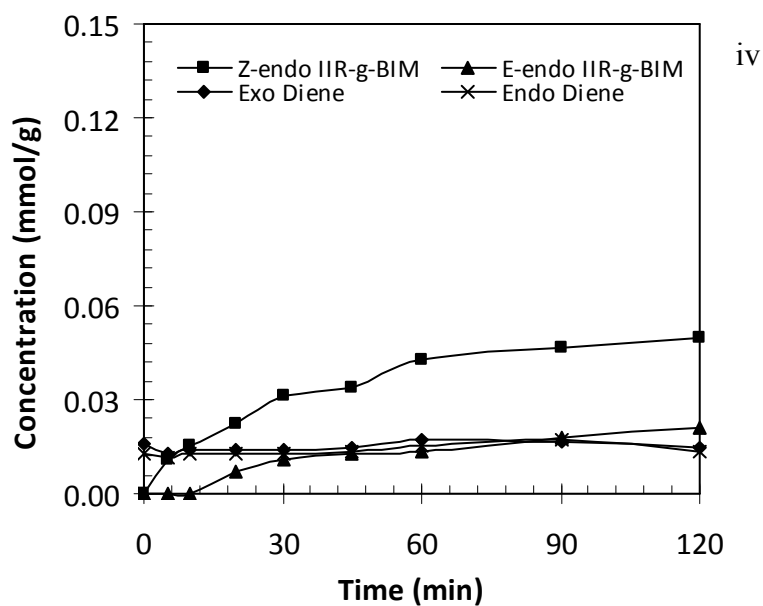
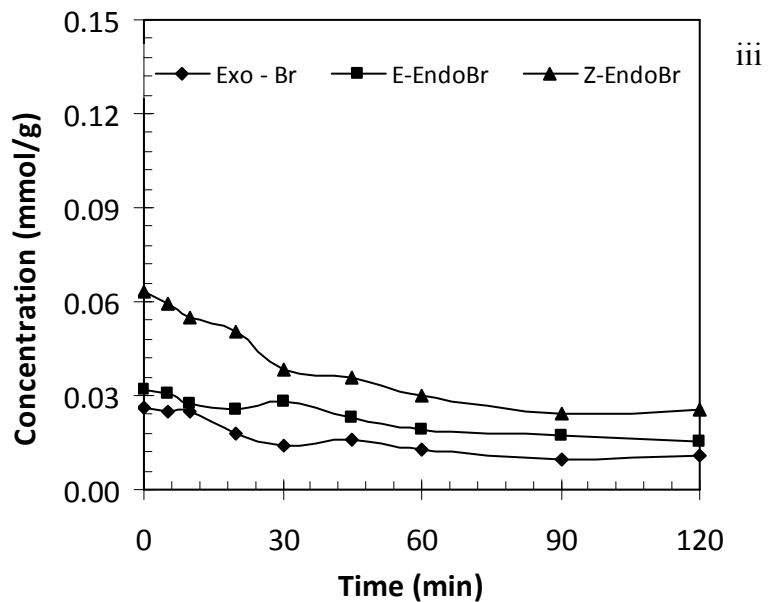


Figure 2.2: Reaction Dynamics of 1-butylimidazole (1.1 equiv) with BIIR in the Haake at 85 °C for 120 minutes. “As received” (i, ii), thermally isomerized (iii, iv) with products on the bottom and reagents on the top

After considerable time, a viable and reproducible solution-based reaction of 6 equivalents of nucleophile was added to a 10 wt% solution of rubber in toluene at 100 °C for 6 hours to get full conversion. As the reactions were done in solution and under a nitrogen gas atmosphere, there was no detectable conjugated dienes (the major side reaction) formation as seen by ^1H NMR; therefore, HBr loss is no longer a concern for the rest of this chapter. Figure 2.3 shows good reaction rates for the system with almost full conversion of the residual brominated isoprene units to the ionic product. As noted above isomerization of bromobutyl rubber was not required as it was not rate limiting, so only “as received” rubber was reacted. The only downside to a solution reaction is that it reacts slower in solution than rubber (due to lower concentration of reagents per volume of reaction medium) and that the material needs to be dried afterwards, which can be difficult at times.

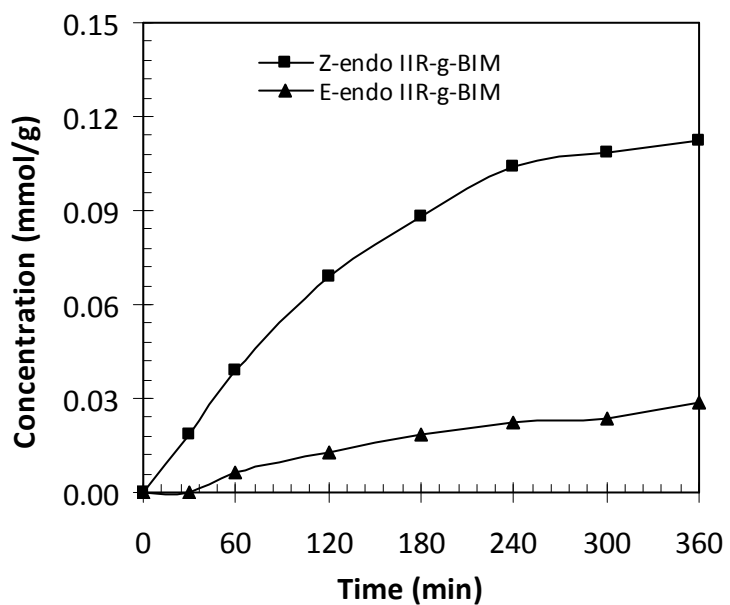
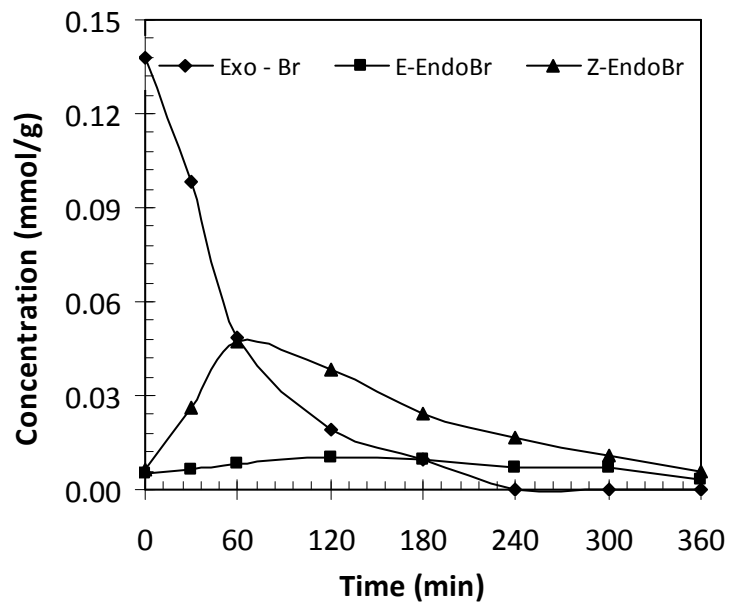


Figure 2.3: Solution state reaction dynamics for 'as received' BIIR in toluene for 6 hours at 100 °C

2.3.3 Varying Ionomer Content

As it has been proven that the 1-butylimidazole ionomer has a reproducible reaction procedure and creates a stable ionomer, more extensive physical tests can be performed. The next area of interest is to investigate at different concentrations of ions in the rubber using the same reaction procedure as outlined in the previous section. This was done by picking appropriate times during the solution reactions to quench the remaining allylic bromide using excess tetrabutylammonium (TBA) acetate, which reacts much faster than the 1-butylimidazole and end the reaction. This procedure allows for a wide range of ionic content available for solution viscosity and rheological testing. The concentrations of ionic content for this report were 0, 11, 34, 77, 84 and 100 mol% of initial allylic bromide in the rubber. The first physical property that was investigated was dilute solution viscosity.

It is well established that ionomers will retain their ion-pair aggregation in solvents of low polarity⁷ and this leads to complex viscosity effects that are dependent on concentration of polymer as well as ion concentration (ionomer content). In dilute solutions (less than 1.0 g/dL), ionomer viscosity is less than the base polymer because of intramolecular ion-pair interactions (Figure 2.4). Intramolecular ionic interaction has been seen to reduce the hydrodynamic radius of the ionomer coils. As ion content increases to above 1.0g/dL, intermolecular forces become dominant, exceeding the critical entanglement concentration C^* where individual chains aggregate to yield a higher viscosity.^{8,9} Intrinsic viscosity or the theoretical zero polymer concentration, is determined by

extrapolating the reduced viscosity of dilute solutions for a certain ionomer content to zero concentration of polymer.

Solution viscosity was done to prove that this material was in fact an ionomer and not a cross-linked material, and also to study varying ion contents. Crosslinked materials would not dissolve in solution and therefore cannot be measured by solution viscosity. It can be seen in Figure 2.4 that intrinsic viscosity decreases as ionomer content increases meaning smaller coils at dilute concentrations of polymer in toluene. Small amounts of ion concentrations changed the properties slightly but become quite substantial when the ionic content reaches a concentration of ionic pairs around 0.12 mmol/g of elastomer.

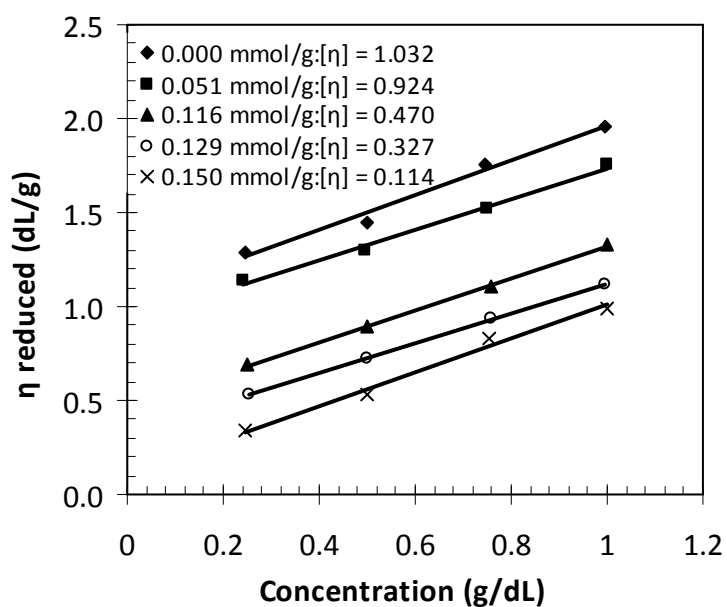
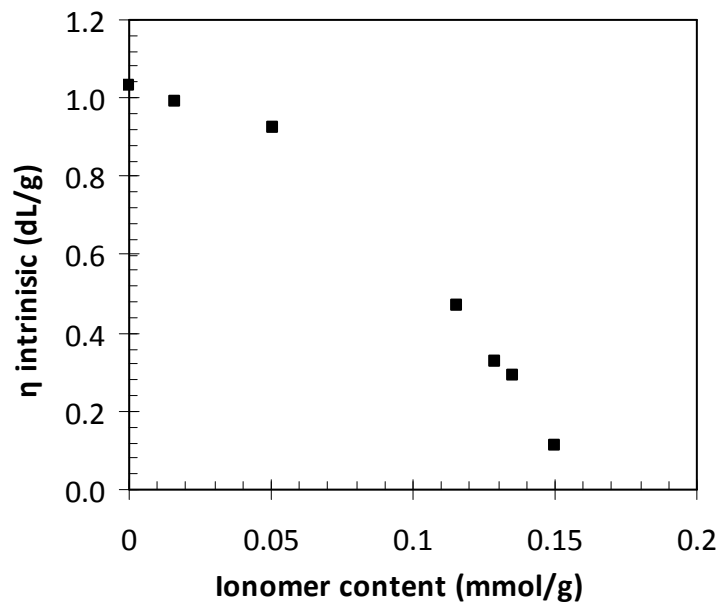


Figure 2.4: Dilute solution viscosity for different ionomer contents (concentration in ionomer content in millimoles per gram of rubber)

The intrinsic viscosity of 0.114 dL/g (Figure 2.5) for fully converted imidazolium ionomer was noticeably lower than the phosphonium ($[\eta] = 0.62$ dL/g) and ammonium

($[\eta] = 0.28 \text{ dL/g}$) based ionomers.³ One of the main reasons for the lower intrinsic viscosity for imidazolium ionomer was that the imidazolium ionomer was reacted in solution, which reduces dehydrohalogenation. The result was more ionic content in the elastomer when compared to solid state where notable amounts of dehydrohalogenations was observed. This would result in a higher content of ionic function in the polymer at full conversion compared with the previous work done by the Parent group. Another possible reason why the imidazolium ionomer had a lower intrinsic viscosity is that toluene might solvate phosphonium and ammonium ionomers better than the imidazolium ionomer.¹⁰ This would create a larger radius of gyration (larger coils) for the same concentration, which would increase the viscosity.

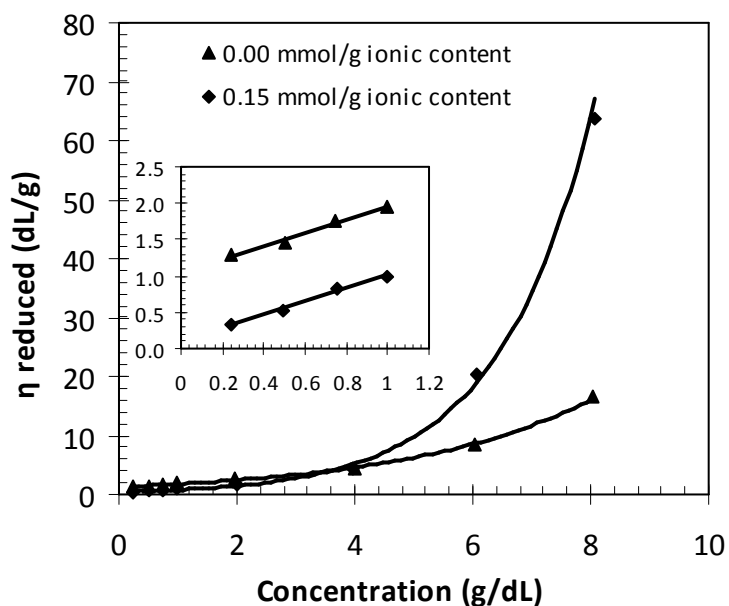


Figure 2.5: Solution viscosity for bromobutyl and fully converted butylimidazolium bromide ionomer. The inset plot is of dilute solution viscosity

Another interesting feature of ionomers, as described above, is that at low concentrations they have very low intrinsic viscosities; however as the concentration increases above the critical entanglement, their viscosity increases greatly. A perfect example of this can be seen in Figure 2.5, where TBA acetate quenched rubber (no ion pairs) has a higher intrinsic viscosity at low concentrations and only slowly increases even at more concentrated regions. In contrast, the ionomer starts much lower at low concentrations and increases exponentially after it passed the critical entanglement concentration, quickly eclipsing the quenched rubber.

There are several properties tests that are usually performed on ionomer systems. These tests included small-angle X-ray scattering (SAXS), glass transition temperature (T_g) and rheology. As previously mentioned in the introduction, there is not enough ionic functionality in the rubber to perform SAXS or T_g , so only rheology was studied. For this project, a temperature sweep from 200 °C to 40 °C followed by the temperature being increased to 200 °C and then back to 40 °C was performed. The first set was to remove any thermal memory in the sample so that the final sweep (200 °C to 40 °C) will be shown in Figure 2.6.

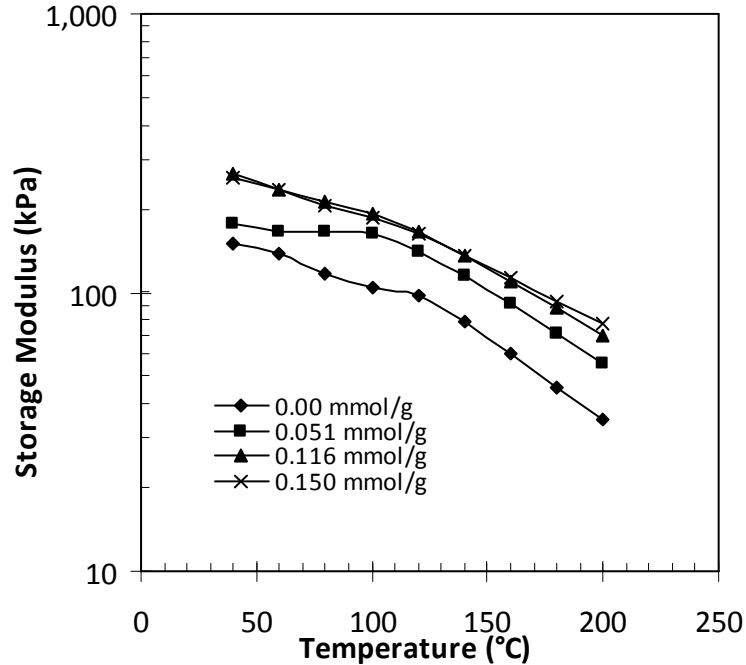


Figure 2.6: Rheology 200 to 40 °C temperature sweep (concentration in ionic content in millimoles per gram of rubber)

From the rheological data (Figure 2.6), there is an increase in modulus as more ionic content is added. This is a known phenomenon, since ionic rubbers have been seen to have similar properties to vulcanizates and would toughen the material. What is interesting is that at around 80% conversion it has the same modulus as the fully converted material. This can be a simple way to have easy cost savings as full conversion is not required to get similar modulus.

From this research it was shown that a small number of ion-pairs lead to a significant increase in properties compared to the base butyl rubber. As the properties plateau as it reaches full conversion, it demonstrates that full conversion is not needed to get adequate property values.

2.3.4 Different nucleophile and electrophile

A brief study into different electrophiles (other halobutyl rubber) and nucleophiles (other alkylimidazole) was done to see if the reaction dynamics would change considerably. This is important as the reaction dynamics are fairly slow with a great excess of 1-butylimidazole being added. The first change in an attempt to increase reactivity to nucleophilic substitution was to change the electrophile from BIIR to brominated poly(isobutylene-co-methylstyrene) (BIMS)(**8**) rubber, with a benzylic bromide content of 0.21 mmol per gram of elastomer. This is a far more reactive specialty rubber and a significant decrease in reaction time is seen in Figure 2.8. The solution reaction occurred at 100 °C with 6 equivalents of 1-butylimidazole and was completed in 3 hours, half the reaction time of the bromobutyl and 1-butylimidazole reactions. Reactions with chlorobutyl rubber were considered but no experiments were done since it is a worse electrophile than bromobutyl rubber.

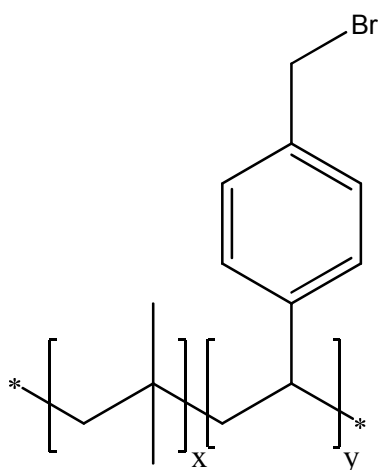
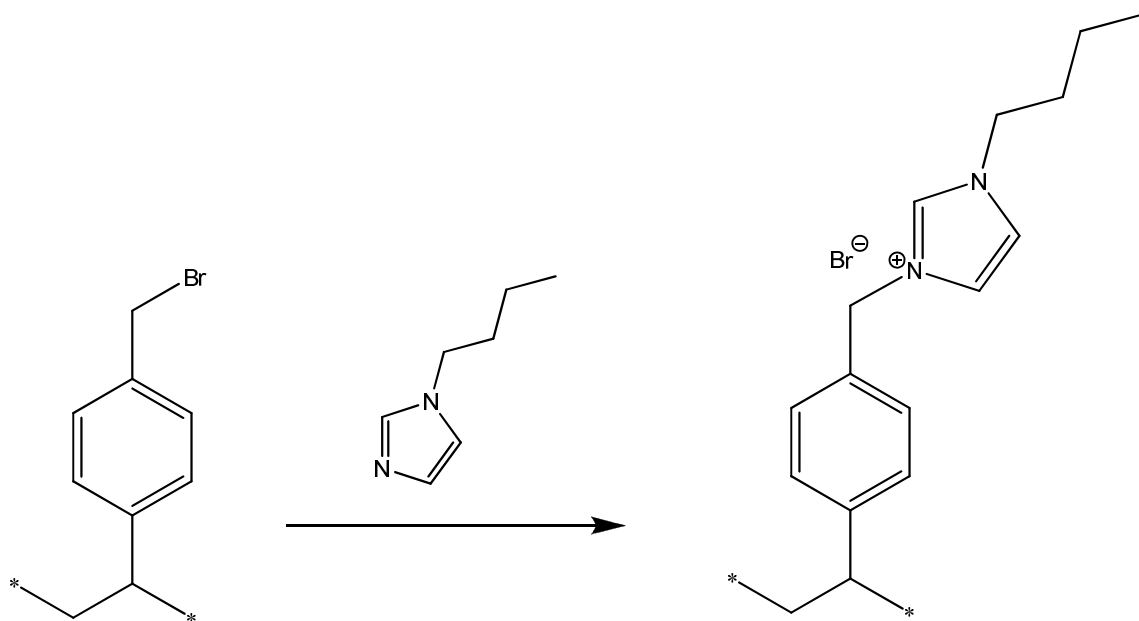


Figure 2.7: Brominated poly(isobutylene-co-methylstyrene) (**8**)

As seen in Figure 2.7, the reason for BIMS elevated reaction rates is the significantly less hindered bromine off of the phenyl group especially when compared to the (exo or endo) bromine in BIIR. As well, BIMS does not need to be treated in anyway for nucleophilic addition as seen in scheme 2.2, and there are no major side reactions or degradation.



Scheme 2.2: N-alkylation of 1-butylimidazole with BIMS

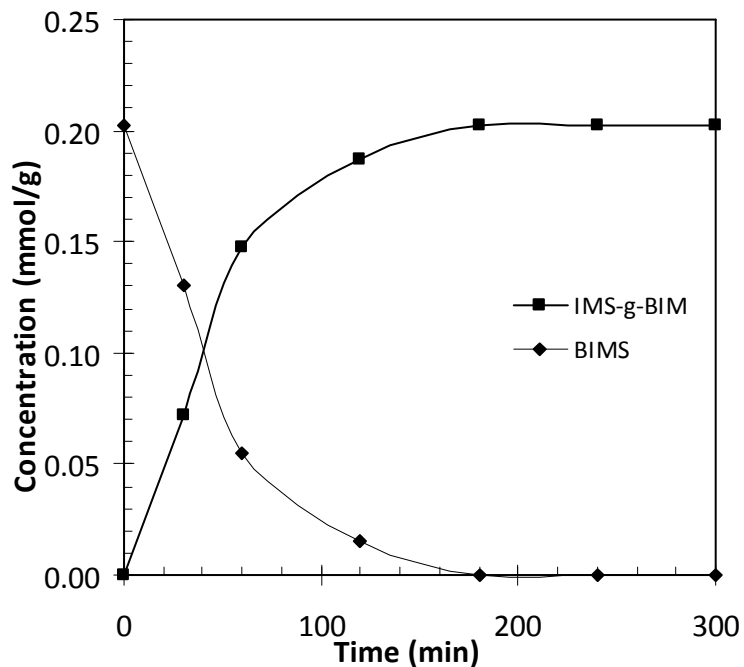


Figure 2.8: Solution state reaction dynamics for as received BIMS reacting with 1-butylimidazole in toluene at 100 °C

One of the problems with commercializing IMS-g-BIM is that BIMS is a specialty product that is not widely produced. This means slightly altering the nucleophile would be the next logical choice. Since the imidazole ring is electron withdrawing, which makes it a poor nucleophile, the addition of a methyl group (an electron donating group) in the 2 position should increase reaction rates. As the same procedure is used as above, 1-decyl-2-methylimidazole was reacted with bromobutyl rubber at 100 °C for six hours with 6 equivalents of nucleophile in toluene. The reaction dynamics for the reaction can be seen in Figure 2.9 and can be compared with Figure 2.3, the same reaction with 1-butylimidazole, and there is no change in reaction rates. Therefore the attempt to add electron density did not work as planned.

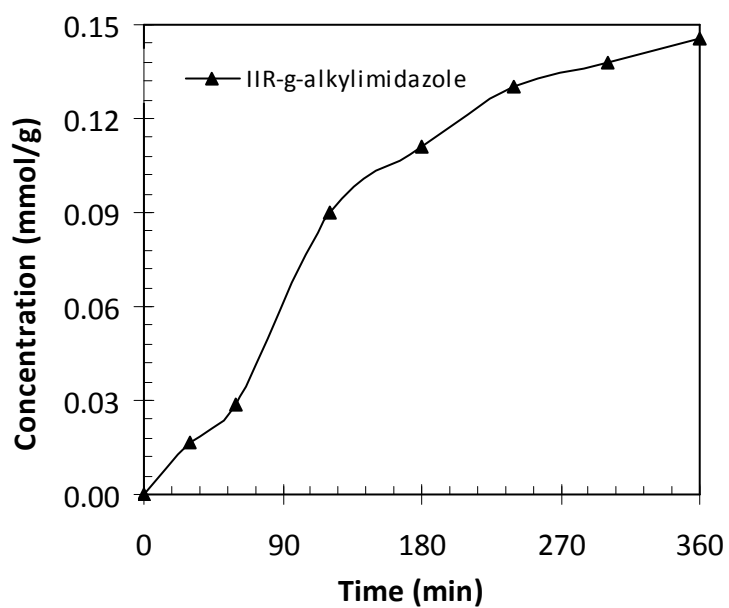
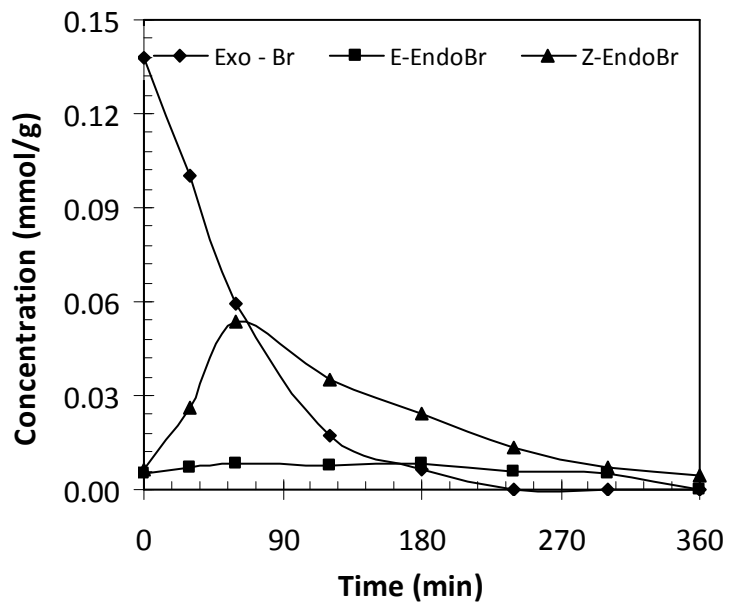


Figure 2.9: Solution state reaction dynamics for as received BIIR with 1-decyl-2-methylimidazole in toluene for 6 hours at 100 °C

2.3.5 Peroxide Cure of 1-Butylimidazole

As there is interest in creating a thermoset imidazolium ionomer, it was necessary to check to see how 1-butylimidazole fared when peroxide cured. This was accomplished by mixing 0.3 wt% of dicumyl peroxide with IIR-g-BIM as well as 0.3 wt% dicumyl peroxide and 1 wt% HVA 2 with IIR-g-BIM and time cured in the APA rheometer at 160 °C as seen in Figure 2.10.

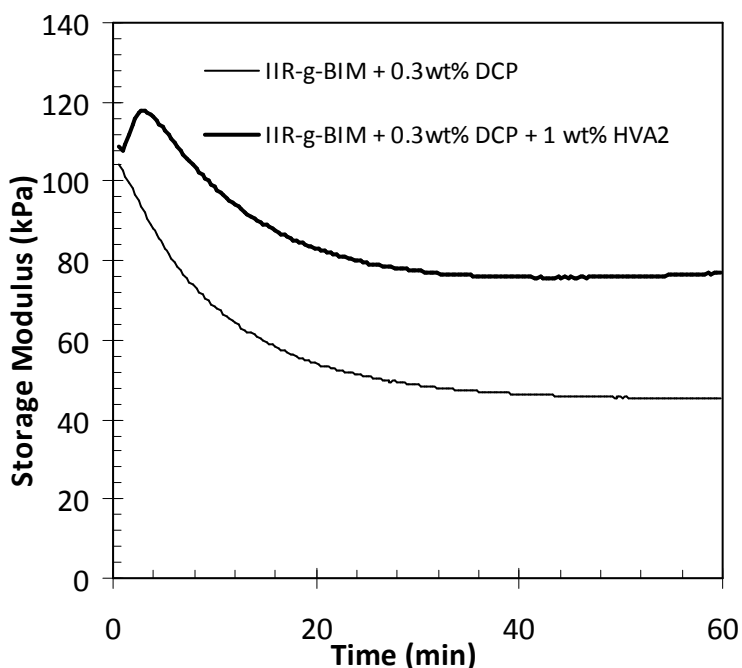


Figure 2.10: Reactions with DCP (left) and DCP and HVA 2 with IIR-g-BIM at 160 °C

In the absence of HVA 2 (the co-agent), chain scission predominates and a significant loss of modulus is noted. When the co-agent is added, the material initially crosslinks, however once the co-agent is consumed, chain scission dominates and a loss of modulus is observed. Therefore 1-butylimidazolium bromide ionomer cannot be peroxide cured to high extent by this formulation.

2.4 Conclusions

Through these studies it was demonstrated that alkylimidazoles are suitable nucleophiles for creating designer ionomers in bromobutyl rubber. The N-alkylation product is stable to reversion as well as nucleophilic exchange with a stronger nucleophile; however, its use outside academia is limited by its lengthy reaction time.

With varying ionomer content, this research determined that full conversion of 1-butyylimidazole with bromobutyl rubber will give the best physical results, but small increases of ion pair content were able to significantly improve the material.

A brief examination of other nucleophiles and electrophiles showed that BIMS was a much better electrophile for 1-butyylimidazole N-alkylation while 1-decyl-2-methylimidazole showed no improvement on 1-butyylimidazole when reacted with BIIR.

The peroxide cure of IIR-g-BIM was poor, with little help from a co-agent. Instead of gaining modulus, the peroxide attacked the exposed methyl group on the isobutylene units causing chain scission. This is a problem that can be overcome by replacing the butyl group in butylimidazole with a functional group that is more reactive to peroxide cure conditions.

2.5 References

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Chapter 3: Preparation of imidazole thermosets with BIIR

3.1 Introduction

Ever since Charles Goodyear first vulcanized rubber, valuable commercial products have been made using cross-linked rubbers including products such as tires, gaskets and inner-tubes. For rubber to be useful for anything other than chewing gum it has to be cross-linked to create a stronger, tougher material that is less prone to tearing and abrasion. Its properties are far superior to both uncured and ionomeric elastomers, which have lower modulus and the ability to cold flow slowly overtime. Vulcanized rubber creates a product that does not undergo any shape changes after curing. For this to be feasible, the compound of rubber, fillers, additives, and cross-linking components must be stable at moderate temperatures (for this section 100 °C is considered moderate) to allow mixing as well as molding. At elevated temperatures (around 160 °C), the materials should crosslink quickly.

Typically, primary amines are used for nitrogen-based cross-linking, while secondary and tertiary amines are used to add functionality to the rubber (tertiary amines produce ionomers as seen in the previous chapter). However, if there are two nitrogens on the same molecule, they can each N-alkylate to form a vulcanizate. If one nitrogen is a tertiary amine, an ionomer can be formed and cross-linking can occur. Ionomers have interesting properties that have been highlighted in the previous sections.

In this chapter, nitrogen-carbon crosslinking bonds will be formed using imidazole derivatives as the crosslinking agent and BIIR (for the most part) as the polymer. As demonstrated in the previous chapter on alkylimidazole, alkylimidazolium salts are stable to both reversion and nucleophile exchange. Therefore, we do not expect any problems with lost modulus once fully cured.

3.2 Experimental

Materials. Brominated 2,2,4,8,8-pentamethyl-4-nonene (BPMN) was prepared as described previously.¹ The following reagents were used as received from Sigma-Aldrich (Oakville, Ontario): 1-butylimidazole (BIM, 98%), 1,4-dibromobutane (99%), imidazole (99%), proton sponge (99%), 1-(2-hydroxyethyl)-imidazole (97%), potassium hydroxide (>90%, flakes) tricaprilmethylammonium chloride (Aliquat ® 336), and succinic anhydride (99+%). Sodium hydroxide (98.1%) was used as received from Fisher Scientific (Fair Lawn, New Jersey). Brominated poly(isobutylene-co-isoprene) (BIIR or BB2030, $M_n = 410\ 000$ and polydispersity = 1.5) containing 0.15 mmol/g of allylic bromide functionality, was used as supplied by LANXESS Inc. (Sarnia, Ontario). Brominated poly(isobutylene-co-paramethylstyrene) (BIMS or Exxpro 3745), containing 0.21 mmol/g benzylic bromide functionality was supplied by Exxon Mobil. Hi-Sil 233 (synthetic hydrated amorphous silica) was used as received from PPG Industries (Pittsburgh, Pa).

Solid State Blending of BIIR + Imidazole + Proton Sponge (9). BIIR (40 g, 6.0 mmol) was blended 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) in a Haake Polylab R600 internal batch mixer equipped with Banbury blades and operating at 90°C and 60 rpm for 5 minutes. The procedure was repeated for 0.25 equiv. of imidazole and 0.5 equiv. of proton sponge; 1.0 equiv. of imidazole and 0.5 equiv. of proton sponge as well as with 0.5 equiv. of imidazole and no proton sponge then 1 equiv. of proton sponge.

Reaction of BPMN with Imidazole (analogous to 9). BPMN (0.02 mL, 0.18 g, 0.148 mmol) was heated for 48 hours at 85°C in toluene- d_8 in a NMR tube to get an equilibrated ratio of E and Z-endo product. The rearranged model compound was then reacted with imidazole (5.05 mg, 74.2 μ mol) and Proton Sponge (15.0 mg, 74.2 μ mol) for 6 hours at 100 °C (to have imidazole above its melt temperature). There was considerable solid build up in the NMR tube so only the toluene- d_8 solution was used. Toluene- d_8 was removed by kugelrohr distillation for 60 minutes at 60-70 °C (P=0.6mmHg) as well as remaining reagent and the product was then dissolved in $CDCl_3$ (for NMR). High-resolution MS analysis required for $C_{28}H_{57}N_2^+$ m/z 457.4521; found m/z 457.4544. Final purified product analyzed by NMR. 1H NMR ($CDCl_3$): δ 0.8-2.2 (m, 2 x $-C(CH_3)_3$, 3 x $-CH_2-$). Found for E-isomer: 1H NMR ($CDCl_3$): δ 4.91 (s, C- CH_2 -N), 5.65 (t, H-C=). Found for Z-isomer: 1H NMR ($CDCl_3$): δ 4.99 (s, C- CH_2 -N), 5.69 (t, H-C=). 2D ROESY 1HNMR was used to differentiate E and Z isomers.

Isomerization of BIIR from exo to endo allylic bromide microstructure. BIIR (40g, 6.0 mmol) was mixed for 120 minutes in the Haake Polylab R600 internal batch mixer equipped with Banbury blades and operating at 115 °C and 60 rpm.

Solid State Blending of Isomerized BIIR + Imidazole + Proton Sponge. Isomerized BIIR (40 g, 6.0 mmol) was blended with 0.5 equivalent imidazole (0.204 g, 3.0 mmol) and 0.5 equivalent proton sponge (0.643 g, 3.0 mmol) in a Haake Polylab R600 internal batch mixer equipped with Banbury blades and operating at 90°C and 60 rpm for 5 minutes.

Solid State Blending of BIMS + Imidazole + Proton Sponge. BIMS (40 g, 8.1 mmol benzylic bromide) was blended with 0.5 equivalent imidazole (0.276 g, 4.05 mmol) and 0.5 equivalent proton sponge (0.868 g, 4.05 mmol) in a Haake Polylab R600 internal batch mixer equipped with Banbury blades and operating at 90°C and 60 rpm for 5 minutes.

Solid State Blending of BIIR and BIM. BIIR (40 g, 6.0 mmol) was blended with 1 equiv. 1-butylimidazole (0.745 g, 6.0 mmol) in a Haake Polylab R600 internal batch mixer equipped with Banbury blades and operating at 40°C and 60 rpm for 5 minutes.

Synthesis of 1,1'(1,4-Butanediyl)bis(imidazole). NaOH (12.50 g) was added to water (12.50 g) to form a 50 wt% solution, and then toluene (60 mL) was added. Imidazole (1.31 g, 19.8 mmol) and tetrabutylammonium bromide (0.606 g, 1.98 mmol) were added

to the solution and stirred at room temperature until all solids were dissolved. 1,4-Dibromobutane (2.02 g, 9.32 mmol) was added to the solution and the mixture was reacted at 60 °C in an oil bath for 16 hours. Solid was observed at the water-toluene interface so 80 mL of water was added and the mixture was stirred at room temperature to produce finer crystals at the bottom and in the aqueous phase. Solids were then collected by vacuum filtration and dried in a vacuum oven. Yield was 1.4857 g (84 % yield). ¹H NMR (CDCl₃) δ 1.76 (t, C-CH₂-CH₂-C), 3.93 (m, N-CH₂-C), 6.86 (s), 7.07 (s), 7.44 (s). mp = 83-86 °C. and mp lit.= 83-86 °C.²

Solid State Blending of BIIR and 1,1'-(1,4-butanediyl)bis(imidazole) (10). BIIR (40 g, 6.0 mmol) was blended with 0.5 equivalent 1,1'-(1,4-butanediyl)bis(imidazole) (0.58 g, 3.0 mmol) in a Haake PolyLab R600 internal batch mixer equipped with Banbury blades and operating at 90°C and 60 rpm for 5 minutes.

Synthesis of 4-[2-(1H-imidazol-1-yl)ethoxy]-4-oxobutanoic acid. 1-(2-hydroxyethyl)imidazole (1.96 g, 0.0178 mol) and succinic anhydride (1.78 g, 0.0178 mol) were added to 20 mL of THF then heated for 6 hours at reflux. Off-white crystals precipitated out of solution and were collected through gravity filtration and dried overnight. ¹H NMR (D₂O) δ 2.34 (t, -CH₂-CH₂-COOR), 2.49 (t, -CH₂-CH₂-COOH), 4.39 (t, -N-CH₂-CH₂-), 4.44 (t, -N-CH₂-CH₂-O), 7.36 (s, -N-CH=CH-N-R) 7.46 (s, -N-CH=CH-N-R), 8.65 (s, -N=CH-N-). High-resolution MS analysis; required for C₁₀H₁₃N₂O₄ *m/z* 212.0797; found *m/z* 212.0802. mp = 108-110 °C.

Reaction of BIIR + 4-[2-(1H-imidazol-1-yl)ethoxy]-4-oxobutanoate with BIIR (11).

4-[2-(1H-imidazol-1-yl)ethoxy]-4-oxobutanoic acid (0.372 g, 1.76 mmol) was mixed with Aliquat 336 (0.710 g, 1.76 mmol) and potassium hydroxide (0.0704 g, 1.76 mmol) for 17 hours at room temperature in toluene (5 mL). The mixture was then added to BIIR (3.57 g, 0.536 mmol) (5 wt% in toluene) and reacted for one hour at 100 °C. BIIR (3.50 g, 0.530 mmol) was then dissolved and mixed in the solution at room temperature to create better dispersion of BIIR and IIR-g-imidazole. Polymeric product was isolated by precipitation in acetone and then re-dissolved in tetrahydrofuran with the polymeric product re-precipitated in acetone. Polymer was then dried under vacuum. Material was milled twice and then dried under high vacuum for 24 hours, this process was repeated and the material was finally milled twice again. Time cure rheology was then performed.

Solid State Blending of BIIR + Imidazole + Proton Sponge + Silica. BIIR (30 g, 4.5 mmol) was blended with 0.5 equivalents of imidazole (0.153 g, 2.25 mmol) and 0.5 equivalents of proton sponge (0.482 g, 2.25mmol) and 30 phr Hi-Sil 233 (9 g) in a Haake Polylab R600 internal batch mixer equipped with Banbury blades and operating at 90°C and 60 rpm for 5 minutes.

Analysis. NMR spectra were recorded with a Bruker Advance-600 spectrometer (600.17 MHz ¹H, 150.92 MHz ¹³C) in deuterated chloroform (CDCl₃) (except where noted otherwise) with chemical shifts referenced to tetramethylsilane.

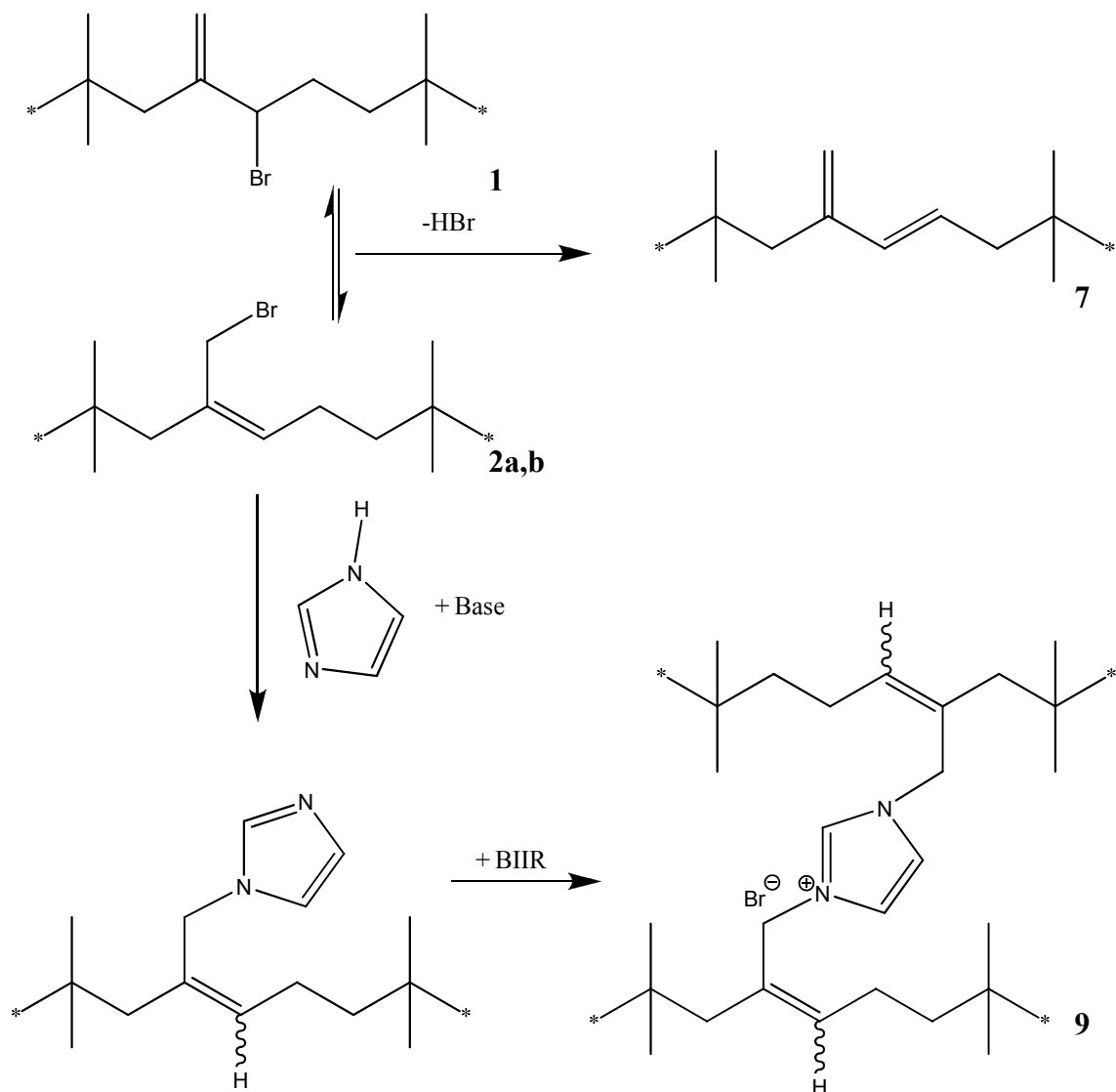
Specific masses for model compound were determined on a Waters/Micromass GC-T TOF mass spectrometer operating in electron impact mode with high-resolution mass spectrometric analysis.

Rheological characterization was carried out with an oscillatory rheometer (Advanced Polymer Analyzer 2000; Alpha Technologies) operating in a parallel plate configuration with a 3 degrees arc at a frequency of 1 Hz.

3.3 Results and Discussion

3.3.1 Structure of imidazolium bromide ionomers

From the previous chapter's work it is apparent that an alkylimidazole reacts reasonably well with bromobutyl rubber to form an ionomer. Since there are several different functional groups that can be added to the imidazole to suit the desired end product, it would be intriguing to determine what happens if no functionality was added at all. Imidazole would produce a bis-alkylated thermoset that becomes an ionomer after two sequential N-alkylations, as seen in scheme 3.1.



Scheme 3.1: N-alkylation of imidazole with BIIR

Our study of the BIIR+imidazole system began with the characterization of products derived from brominated 2,2,4,8,8-pentamethyl-4-nonene (BPMN). This compound has proven to be an accurate model for the allylic bromide functionality within BIIR,³ and it provides the unambiguous structural data that is difficult to acquire for chemically modified polymers, and impossible to obtain for thermoset materials. Consider the ¹H-

NMR spectra illustrated in Figures 3.1 for the BPMN-derived allylic imidazoles, where both Z and E bromomethyl isomers are seen. It is evident that the imidazole group in the middle blocks the coupling of the allylic chains so only two variations are seen even though three isomeric structures are possible.

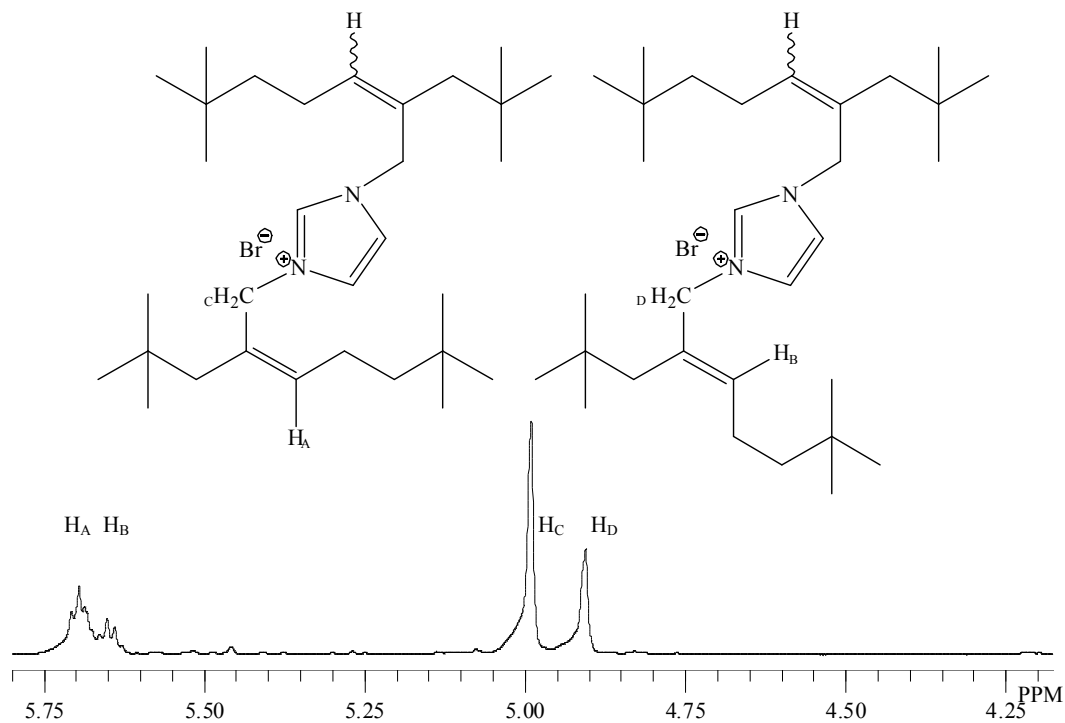


Figure 3.1: ^1H -NMR of model compounds for bis-alkylated imidazole with BPMN

Having characterized the main reaction product shown in Figure 3.1, studies shifted to the dynamics of these cures, starting with the simple BIIR + imidazole approach. For this strategy to be commercially viable, cross-linking must be avoided during the compound mixing process, which can reach temperatures above 100°C due to mechanical shear. Furthermore, the onset of cross-linking at a designated cure temperature such as 160°C should be delayed slightly to allow the compound to assume the shape of the compression

mold cavity before curing. Thirdly, the cross-linking rate beyond this delayed onset should be rapid enough to yield the cured article in a reasonably short batch time. Each experiment summarized in Figure 3.3 was comprised of two phases in the rheometer: a 20 minute period at 100°C, followed immediately by 40 minutes at 160°C. In every case, the modulus of compounds comprised of BIIR, imidazole, and Proton Sponge was stable at 100°C, and reduced steadily upon heating to 160°C for about 3 min (relaxation), which marked the onset of an imidazole-derived cure.

Since imidazole produces a thermoset product, the only way to mix it is to compound it in the solid state, in this case in a Haake batch mixer at 90 °C for five minutes. Since the melt temperature of imidazole is 89-91 °C (slightly higher temperatures in the mixer are seen during mixing from friction inside the bowl), it was important to have it melted so that it would provide good dispersion in the blend. Throughout this chapter, imidazole contents will be reported as molar equivalents relative to the 0.15 mmol of allylic bromide found in every gram of BIIR.

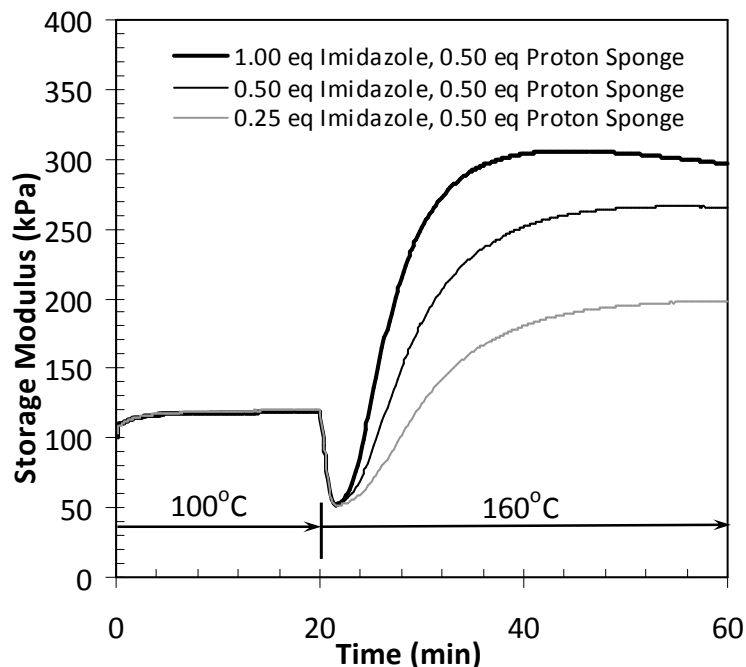


Figure 3.2: Cross-linking dynamics of BIIR and varying amounts of imidazole

Figure 3.2 illustrates the effect of imidazole concentration on cure rates and yields. As expected, increasing imidazole availability from 0.25 equivalents to 0.50 (the stoichiometric amount) raised the cure rate and extent. Going beyond the stoichiometric requirement to 1.00 eq of imidazole raised the modulus further, owing to a more competitive N-alkylation rate relative to BIIR dehydrobromination. When heated at 160°C in the absence of imidazole, 19% of the allylic bromide within BIIR was converted to conjugated diene within 10 min, and 43% was converted after 20 min (in the Haake).⁴ Clearly, higher nucleophile concentrations promote cross-linking by directing allylic bromide conversion toward diallylimidazolium bromide at the expense of conjugated diene.

The inclusion of Proton Sponge (1,8-bis(dimethylamino)naphthene) in an imidazole formulation serves to scavenge hydrogen bromide. Bromobutyl rubber is fairly sensitive to dehydrohalogenation that forms conjugated dienes plus HBr, which is an undesirable side reaction that can consume significant amounts of allylic bromide at 160°C. Fortunately, evidence suggests that this reaction proceeds through an E₁ elimination mechanism, and is unaffected by strong base.¹ Therefore, the requisite base can be selected without concern for loss of allylic bromide to conjugated diene byproducts. From Figure 3.3, it can be seen that the addition of proton sponge increases the cure as less conjugated dienes are formed. It also shows that the addition of more Proton Sponge than stoichiometric amounts does not increase the cure noticeably, which would indicate the N-alkylation of the imidazole is faster than the thermal dehydrohalogenation.

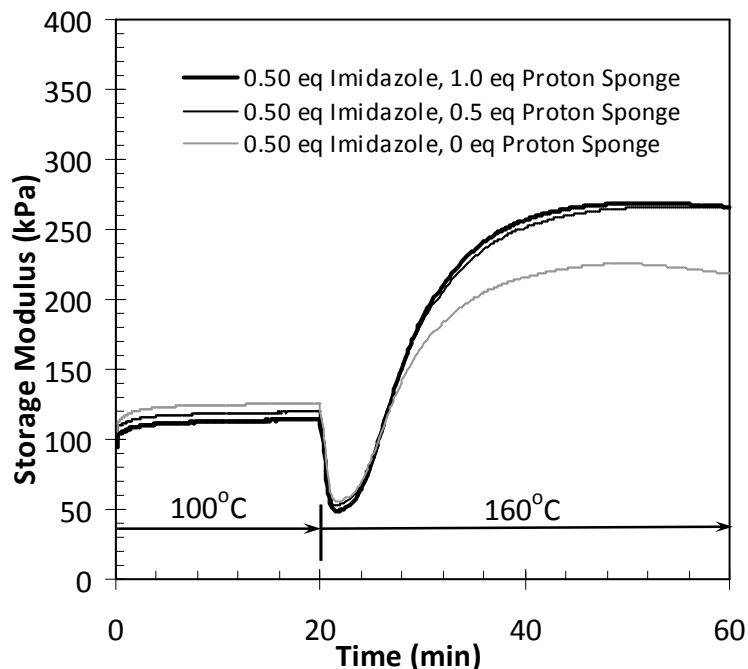


Figure 3.3: Cross-linking dynamics with 0.5 equiv of imidazole and varying Proton Sponge

While Proton Sponge is a powerful base for HBr, it is important to note that epoxides and calcium stearate are added to commercial grades of BIIR to stabilize against HBr-catalyzed polymer degradation. As such, additional base is not an absolute requirement for the imidazole reactions of present interest, but it does help significantly as there is insufficient base in the system as seen in Figure 3.3 when no Proton Sponge is added. This improvement is attributed to the superior basicity and solubility of Proton Sponge in the elastomer matrix, which limits the extent of imidazole protonation.

The dynamics of the imidazolium thermoset formation provide the requisite inactivity at 100°C, as well as the desired delayed onset and cure rates at 160 °C. This superior performance is due, in small part, to the latency of the allylic bromide within BIIR.

Consider the rheometry data presented in Figure 3.4, which compares imidazole cures of “as received” BIIR containing 95:5 ratio of exomethylene (**2**) : bromomethyl (**3a,b**) functionality, “isomerized” BIIR containing a 10 : 90 ratio of exomethylene : bromomethyl, and brominated poly(isobutylene-co-paramethyl styrene) (BIMS) that contains 0.21 mmole of benzylic bromide functionality per gram of polymer. BIMS was excessively reactive at 100°C, and provided no scorch protection at 160°C. Although the sterically unencumbered benzylic bromide is too reactive toward imidazole, its stability toward dehydrohalogenation provides higher ultimate cure extents than BIIR, whose cure yields are impacted negatively by HBr elimination. BIMS was also expected to have a higher modulus as it has 40% more bromine than BIIR. Isomerized bromobutyl rubber has an increased reaction rate compared to “as received” BIIR, because, Z,E bromomethyl isomers are more reactive than the exomethylene isomer. However, due to conjugated diene formation during the isomerization step, there is a significant loss of final modulus.

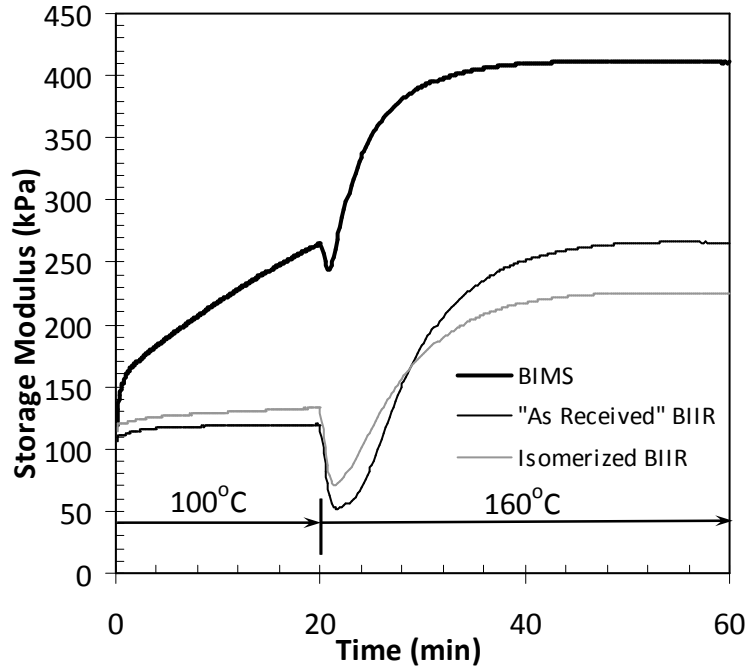


Figure 3.4: Cross-linking dynamics of “as received” BIIR; Isomerized BIIR + Imidazole; BIMS + Imidazole

3.3.2 Compounding 1-butylimidazole with BIIR

As a brief comparison of reaction dynamics for compounded imidazole with BIIR and 1-butylimidazole with BIIR can be seen in Figure 3.5. Stoichiometric amounts and half an equivalent of 1-butylimidazole were compounded in bromobutyl rubber at 40°C for 5 minutes in the Haake batch mixer. The lower temperature were used because the 1-butylimidazole reacted quite readily at 90 °C and was reacting during compounding. As 1-butylimidazole is a liquid at room temperature (unlike imidazole which is a solid), dispersion into the rubber media was not an issue.

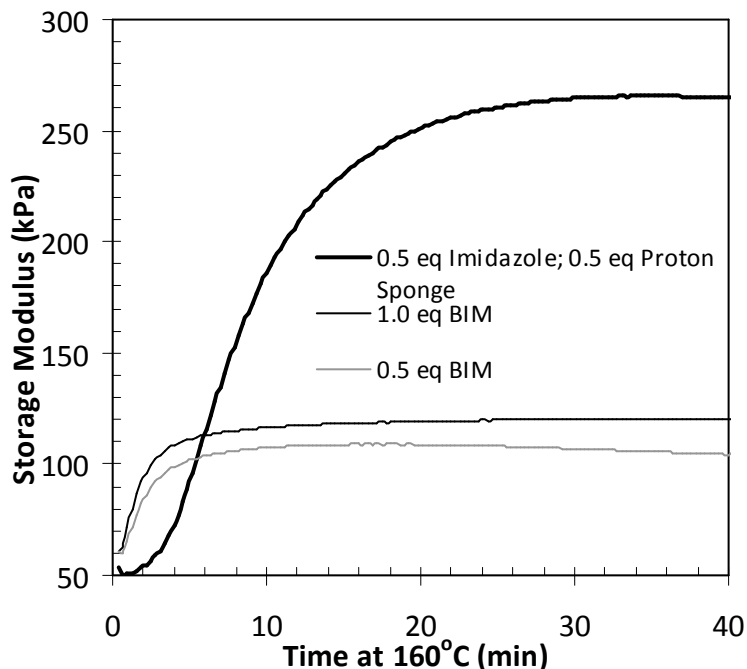


Figure 3.5: Comparison of butylimidazole to BIIR+imidazole at 160 °C

It is quite apparent that 1-butylimidazole reacts much faster than imidazole and plateaus much sooner and at a much lower modulus. The reason imidazole cures slower is because it needs to N-alkylate twice whereas 1-butylimidazole reacts only once to form an ionomer. As noted from previous 1-butylimidazole work, the maximum ion pair content yields the highest results however 0.5 equivalents of the required amount yields comparable modulus. However, as not all allylic bromide is consumed with half an equivalent of 1-butylimidazole, there is noticeable degradation from HBr. This is also an excellent example of vulcanizates versus ionomers at elevated temperatures. The vulcanizate reaches a decent modulus, while the modulus of the ionomer is quite low. This stems from the ionomer softening and the restricted chain mobility region disappearing at elevated temperatures.⁵

3.3.3 Silica-filled systems

Silica is a filler that can be used to reinforce polymer materials if it is properly dispersed in the polymer matrix. Ionomers have been shown to disperse silica very well in butyl rubber compared to BIIR which it is non-reinforcing.⁶ Here the effect of forming an ionomer after silica addition would make on reinforcement will be questioned.

So that the filled system could be compared to the imidazole systems from above, 0.5 equivalents of imidazole and Proton Sponge were added to BIIR in a Haake batch mixer along with 30 phr of Hi-Sil 233 for 5 minutes at 90 °C. As with the BIIR + imidazole systems, there was no curing during the mixing period (100 °C). Both plots are compared in Figure 3.6.

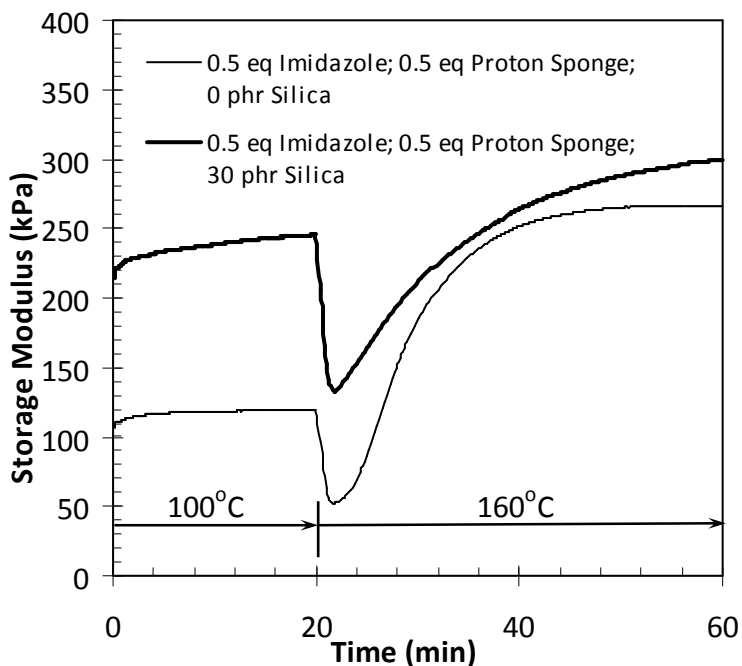


Figure 3.6: Cross-linking dynamics of BIIR + Imidazole; silica filled BIIR + Imidazole

As imagined, the filled system has a higher modulus and toughness than the rubber and imidazole system. There are relaxation effects at 100 °C as the material aligns to its new environment. Also, it is easy to identify that the silica does not reinforce the material and hinders the cure considerably so that the material does not reach full conversion after 40 minutes at 160 °C. Therefore, if imidazolium-based thermosets are going to be useful for filled systems, they must be ionomers first and then cured after silica addition for best silica dispersion.

3.3.4 Bis-imidazole

Imidazole reacting with bromobutyl rubber was successful as it provides good scorch protection at low temperatures and then good cures at elevated temperatures. So other thermoset derivatives of imidazole were considered to examine different properties of these materials. One such derivative is a bis-imidazole, which is two imidazole rings connected by a carbon chain off of a nitrogen atom. The bis-imidazole that was used for the experiments was (1,1'(1,4-butanediyl)bis(imidazole)) as seen in Figure 3.7. The concept is that the bis-imidazole will N-alkylate twice as imidazole did to form a thermoset; however each N-alkylation would form an ionomer. In theory, there would be twice as much ionic content as in the thermoset imidazolium ionomer.

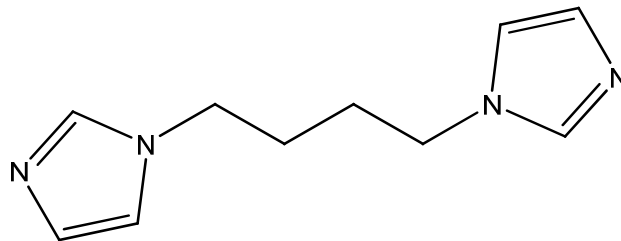
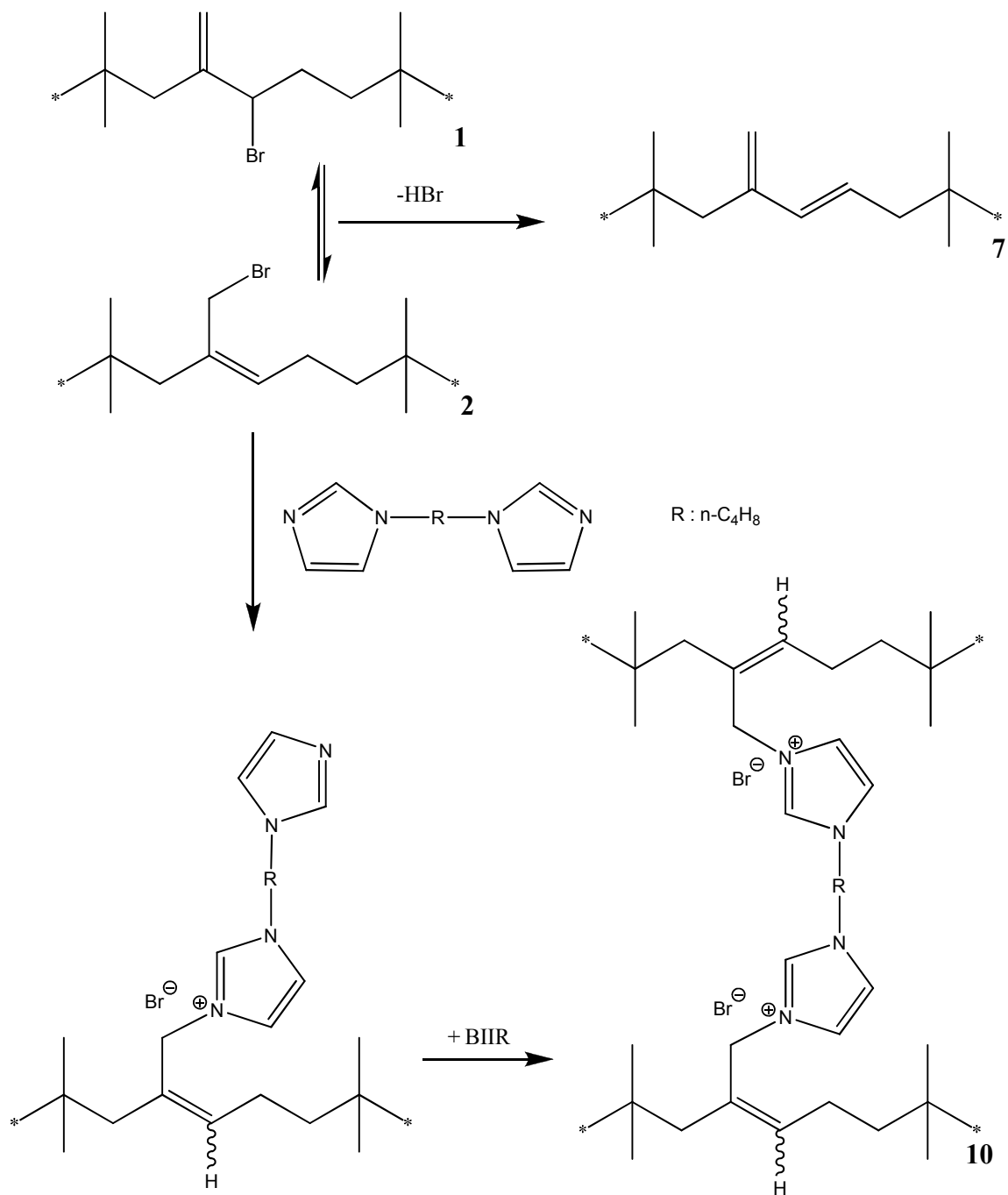


Figure 3.7: 1,1'-(1,4-Butanediyl)bis(imidazole)

The bis-imidazole was compounded into the rubber at 90 °C in a Haake batch mixer because, it and the imidazole have similar melting points. However it does not require any Proton Sponge or base of any kind. Reaction scheme can be seen in scheme 3.2.



Scheme 3.2: Reaction scheme of N-alkylation of bis-imidazole with BIIR

Bis-alkylated bis-imidazole was compared to imidazole using the time sweep temperature step as explained in the previous section, and can be seen in Figure 3.8.

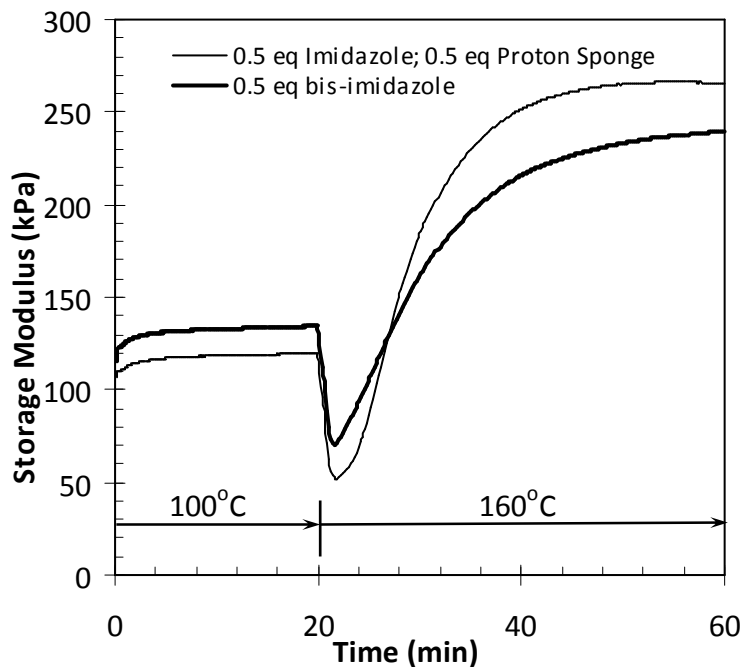


Figure 3.8: Cross-linking dynamics of BIIR + Imidazole; BIIR +bisimidazole

Bis-imidazole reacting with BIIR had similar scorch protection to the imidazole however it reacts slower at 160 °C and achieves a lower maximum modulus. One reason this could have happened was that after the first alkylation, it forms an ionomer: the ionomer will tend to form ionic aggregation which would make it harder for the second imidazole to react with a second allylic bromide.

3.3.5 IIR-g-imidazole

A drawback of the thermoset chemistry described above is the need to handle hazardous imidazole using a conventional polymer compounding device. An attractive variation involves the complete conversion of allylic bromide to pendant imidazole functionality to give IIR-g-imidazole (IIR-g-IM), which can be mixed with BIIR to yield a masterbatch

that is free of hazardous imidazole, but provides an imidazolium thermoset upon heating to conventional curing temperatures. As a result, IIR-g-imidazole can serve as a macro-imidazole reagent capable of yielding a thermoset when combined with an equal amount of BIIR. Attempts in preparation of IIR-g-imidazole using trimethylsilylimidazole were unsuccessful as the TMS group departed prematurely with free bromide. This allowed for 4-[2-(1H-imidazol-1-yl)ethoxy]-4-oxobutanoate anion which has two competing nucleophiles (the carboxylate and the imidazole), with the imidazole, which reacts much slower and therefore produced a grafted imidazole. This material can then be mixed with BIIR and cured.

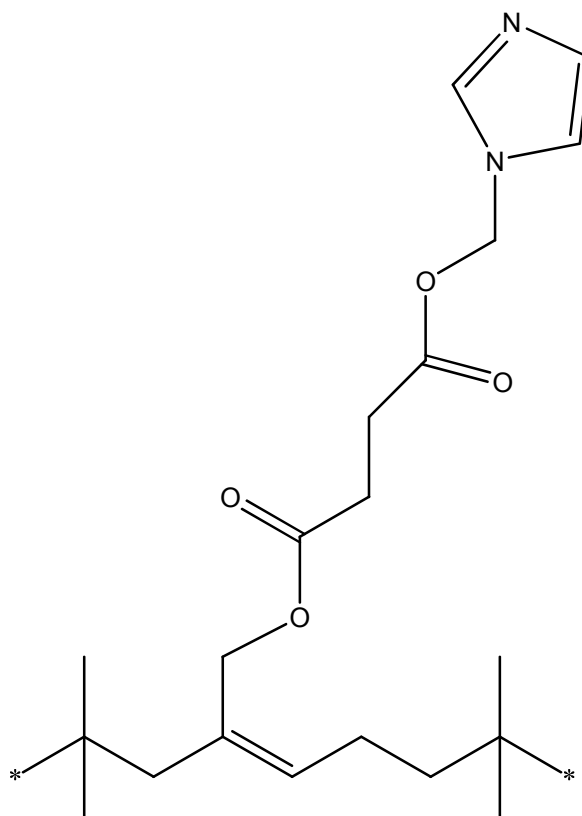


Figure 3.9: BIIR + 4-[2-(1H-imidazol-1-yl)ethoxy]-4-oxobutanoate (11)

The carboxylate imidazole derivative had issues of its own when trying to react it with bromobutyl rubber. As the reaction needed to occur in solution so that the system could more easily be controlled (two competing nucleophiles), the carboxylate imidazole was required to be soluble in toluene (the solvent of choice). The imidazole compound was soluble in polar solvents; however, the rubber is soluble in non-polar solvent. A phase transfer catalyst was required. Previous work done by the Parent group showed that tetrabutylammonium ion (TBA) was a good cationic phase transfer catalyst for rubber.⁷ However, for this imidazole compound, the TBA did not provide adequate solubility in toluene. A larger, more bulky cation was required, so Aliquat ® 336 was used. With this larger phase transfer catalyst, the reaction went well at 100 °C for 1 hour. There were small amounts of gel due to competing reaction, but, the rubber product was soluble in CDCl₃ with a few violent shakes of the vial. The IIR-g-imidazole product was then mixed with BIIR in solution to provide the best mixing and dispersion. Drying procedures were the same as with the 1-butyylimidazolium bromide ionomer. Rheological data of a time sweep with a temperature step can be seen in Figure 3.10.

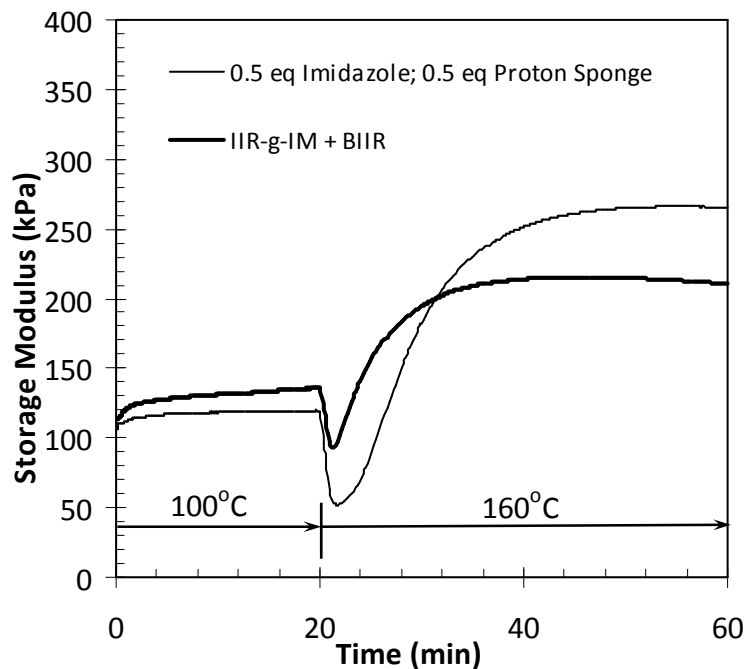


Figure 3.10: Cross-linking dynamics of BIIR + Imidazole; silica filled BIIR + IIR-g-IM

From the data, it is apparent that the grafted imidazole does not have the same scorch protection as the imidazole as it starts reacting faster than imidazole. It is interesting that the grafted imidazole and the free imidazole have the same reaction rates during the cure period (the linear portion), but, however the grafted imidazole has less delay. This is probably because imidazole needs to alkylate twice while the grafted imidazole only reacts once. Therefore, the delay in curing for the free imidazole is from the first alkylation which does not affect modulus, and once the second alkylation occurs the modulus increases substantially.

3.4 Conclusion

It was a pleasant surprise to see that imidazole had such great scorch protection at low temperatures, and then good cure at higher temperature. It was apparent that adding more imidazole would increase reaction rates and modulus, although it was not stable: adding less than stoichiometric amounts of imidazole yielded a cure with a lower modulus and degraded. Also the addition of excess Proton Sponge did not increase the cure; however, no Proton Sponge saw a marked decrease in reaction rate and modulus due to conjugated diene and unchecked HBr formation.

Since the reaction with stoichiometric amounts of imidazole and Proton Sponge worked so well with “as received” bromobutyl rubber, isomerized bromobutyl rubber and BIMS were also tried. BIMS yielded no scorch protection however it did produce a very high modulus. Isomerized rubber reacted slightly faster than “as received” rubber however never reached the same modulus due to conjugated dienes from the pre-compound step.

The butyl-rubber grafted imidazole reaction with BIIR demonstrated that there is considerable time between the first N-alkylation and the second thermoset forming reaction. This is important industrially as it provides time for the rubber to enter the mold.

3.5 References

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Chapter 4: Conclusion and Future Work

4.1 Conclusion

The quaternization of alkylimidazole with bromobutyl rubber was successful in forming a non-reversible ionomeric elastomer that was stable to nucleophilic substitution. The only drawback was that the reaction required a large excess of nucleophile and several hours in solution to reach full conversion.

Varying ionic content in the rubber demonstrated that adding a small amount of ionic functionality was able to have a large effect on physical properties. From solution viscosity and rheology, it was demonstrated that increasing ionic functionality above eighty percent (of initial allylic bromide content) yielded similar results to the fully converted ionomer.

Imidazole-based thermosets can be prepared using imidazole-derivates and brominated butyl rubber. Stoichiometric amounts of both imidazole and proton sponge (the base) produced the optimal results. Excess imidazole reached a higher modulus but it degraded over time, and while the importance of additional base was noted when no proton sponge was added. BIMS had no scorch protection and a very high modulus when crosslinked with imidazole and base. Alkylimidazole reacts faster than imidazole; however, it does not reach the same modulus at high temperatures due to relaxation in the restricted mobility areas in the ionomer.

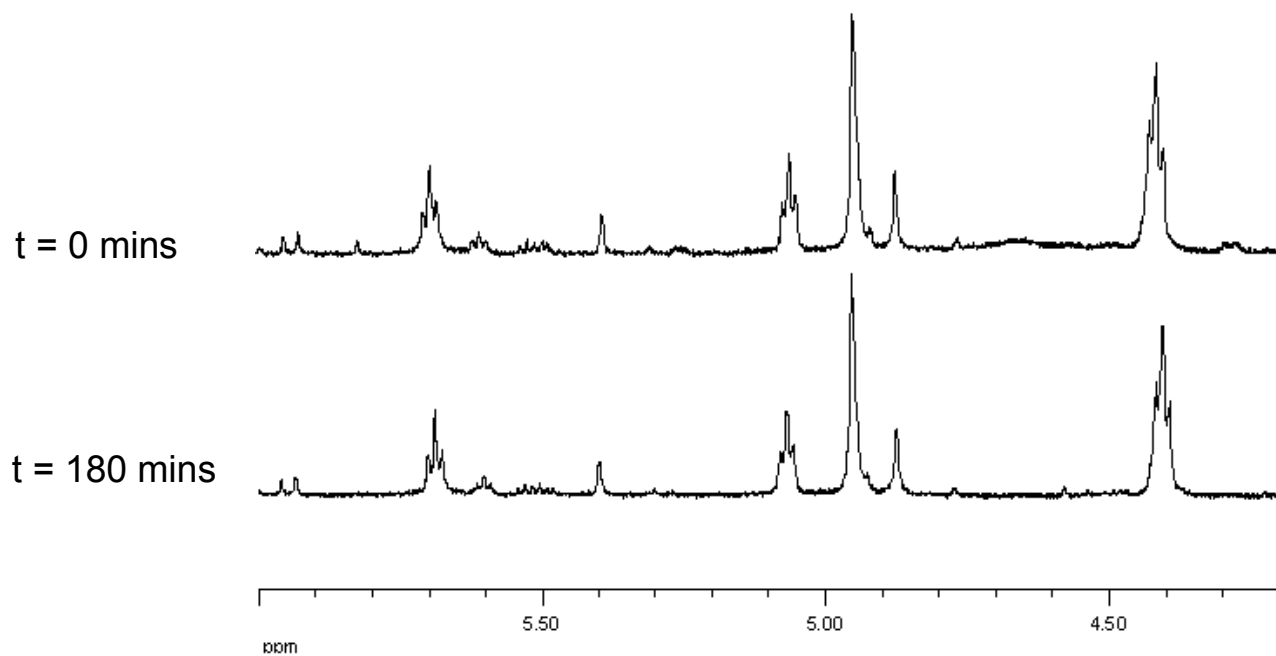
Grafting an imidazole derivative to brominated butyl rubber to create an elastomer with a pendant imidazole was successful as a proof of concept. It did not have the same scorch protection as imidazole, but it removed hazardous free imidazole from the system for possible commercial applications.

4.2 Future Work

As alkylimidazolium bromide salts have been noted as antimicrobials, further studies of the antimicrobial properties of the 1-butylimidazolium bromide ionomer are warranted, as are studies on structural variants in which the length of the alkyl chain is altered.

For thermoset imidazolium rubber, research on its physical properties would be of interest. Since reaction dynamics and cure studies have already been performed, other tests - mostly for automotive purposes such as tensile, flexural, and abrasion - should be performed.

Appendix A



Downfield region of the ^1H NMR spectra (CDCl_3) of the stability test of IIR-g-BIM when reacted with 1.5 equivalents of tetrabutylammonium acetate for three hours at $100\text{ }^\circ\text{C}$. No changes in chemical shifts were noted.