

**Reactive Ionomers: N-vinylimidazolium Bromide Derivatives of
Poly(isobutylene-*co*-isoprene) and Poly(isobutylene-*co*-*para*-
methylstyrene)**

by

Adam Michael Ozvald

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Abstract

Ionomers bearing reactive ion-pair functionality are a novel class of materials that have been prepared. The N-alkylation of N-vinylimidazole by poly(isobutylene-*co*-isoprene) produced the reactive ionomer product in good yield, through a solvent-borne process. Solvent-free conditions can also be used to produce reactive ionomers by the N-alkylation of N-vinylimidazole by poly(isobutylene-*co*-*para*-methylstyrene). Characterization of these derivatives was carried out with the assistance of model compounds, and showed excellent agreement with ^1H NMR spectra.

These reactive ionomers readily crosslink with peroxide at elevated temperatures and in the absence of peroxide they have excellent thermal stability. The amount of crosslinking can be altered based on the vinyl content of the material, to target various applications. N-alkylation of N-vinylimidazole can be carried out concurrently with a non-reactive N-alkylimidazole to achieve desired vinyl contents and tailor the physical properties of these materials. These materials contain both ionic and covalent crosslink networks, and this hybrid network structure provides these materials with unique crosslink structures and stress relaxation properties.

Conventional rubber fillers are compatible with these novel reactive ionomers. Carbon black and precipitated silica have no adverse effects on the peroxide crosslinking of the elastomers and a constant peroxide loading can be used regardless of the filler loading. Payne analysis shows good filler dispersion at low filler loading; however, there is some evidence of reticulate filler network formation at high filler loadings.

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Abbreviations

BIIR – brominated poly(isobutylene-*co*-isoprene)

BIMS – brominated poly(isobutylene-*co-para*-methylstyrene)

BHT – butylated hydroxytoluene or 2,6-di-*tert*-butyl-4-methylphenol

BPMN – brominated 2,2,4,8,8-pentamethyl-4-nonene

BuIm – N-butylimidazole

δ - chemical shift

dd – doublet of doublets

DCP – dicumyl peroxide

DDI – dodecyl itaconate

$\Delta G'$ – change in storage modulus

DSC – differential scanning calorimetry

eq. – molar equivalents

Exo-Br – exomethylene derivative of BIIR

g – grams

G' – storage modulus

G'' – loss modulus

h – hours

HBr – hydrogen bromide

Hz – Hertz

IIR – poly(isobutylene-*co*-isoprene)

IMS – poly(isobutylene-*co-para*-methylstyrene)

IIR-BuImBr – N-butylimidazolium bromide derivative of BIIR

IIR-DDI – dodecyl itaconate derivative of BIIR

IIR-NR₃Br – N-alkylammonium bromide derivative of BIIR

IIR-PPh₃Br – Triphenylphosphonium bromide derivative of BIIR

IIR-VImBr – N-vinylimidazolium bromide derivative of BIIR

IMS-BuImBr – N-butylimidazolium bromide derivative of BIMS

IMS-NR₃Br – N-alkylammonium bromide derivative of BIMS

IMS-PPh₃Br – Triphenylphosphonium bromide derivative of BIMS

IMS-VImBr – N-vinylimidazolium bromide derivative of BIMS

kg – kilograms

mL – milliliter

M_n – number average molecular weight

mm – millimetres

MS – mass spectrometry

mol – moles

MPa - megapascals

MeOH – methanol

mmol – millimoles

NMR – nuclear magnetic resonance

NR₃ – trialkylamine

PIB – poly(isobutylene)

ppm – parts per million

PMN-VImBr – N-vinylimidazolium bromide derivative of BPMN

PPh₃ – triphenylphosphonium bromide

q – quartet

ROOR – peroxide

s – singlet

S_N2 – bimolecular nucleophilic substitution

S_N2' – abnormal bimolecular nucleophilic substitution

t – triplet

T_g – glass transition temperature

$t_{1/2}$ – half life

$\tan \delta$ - loss tangent (G''/G')

TBAB – tetra-N-butylammonium bromide

TBAAc – tetra-N-butylammonium acetate

TBAOH – tetra-N-butylammonium hydroxide

VIm – N-vinylimidazole

wt% - percent by mass

XL - crosslinked

Chapter 1: Introduction and Literature Review

1.1 The Structure and Utility of Isobutylene-rich Elastomers

Poly(isobutylene) (PIB, Figure 1.1), is an amorphous homopolymer with a glass transition temperature on the order of $-60\text{ }^{\circ}\text{C}$. Commercial grades of this elastomer have molecular weights in the range of 100 kg/mole, giving typical uncrosslinked elastomer properties such as high elongation at break and low stiffness (Young's modulus). The polymer provides exceptional thermal and oxidative stability, unique vibration dampening qualities, and superior resistance to gas permeability.¹ As such, PIB is useful for variety of products, including adhesives, sealants and chewing gums.

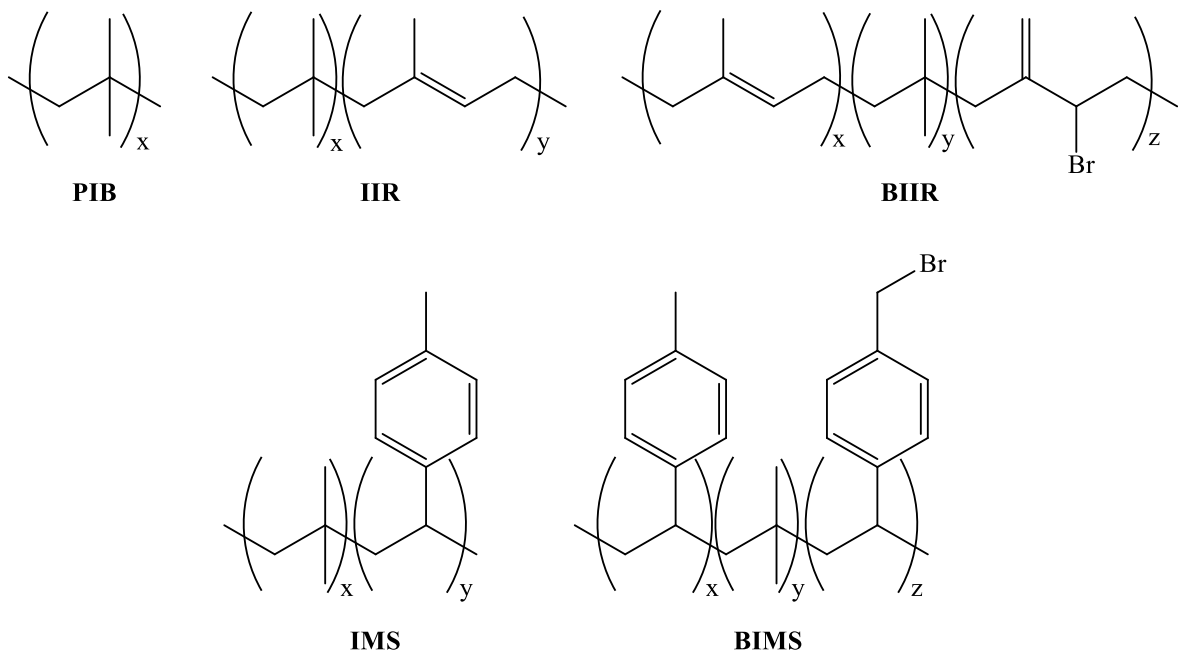


Figure 1.1: The Structures of Isobutylene-rich Elastomers

One limitation of PIB is its poor reactivity towards crosslinking. Uncrosslinked rubber is a viscoelastic material that deforms irreversibly under an applied stress and, as such, it is not a useful engineering material. Vulcanization, also known as curing or crosslinking, generates a covalent network between polymer chains (Figure 1.2), such that chain segments cannot relax when the rubber article is subjected to a sustained load.¹ This improves the modulus, tensile failure properties, and long-term creep resistance of the polymer, allowing it to be used in a wide range of consumer goods. Modulus is a measure of stiffness and can be resolved into two components based on the stress response to an applied sinusoidal strain. The in-phase stress response is called the storage modulus (G') and the out-of-phase stress response is called the loss modulus (G''). Storage modulus reflects the elastic component and loss modulus reflects the viscous component of a polymer's response to an applied strain. The physical properties of a viscoelastic material contain contributions from both the storage and loss moduli. The ratio of the loss modulus to the storage modulus is termed the loss tangent and is calculated by:

$$\tan \delta = \frac{G''}{G'}$$

An ideal elastic solid has a $\tan \delta$ value of zero and an ideal viscous liquid has a $\tan \delta$ value approaching infinity.²

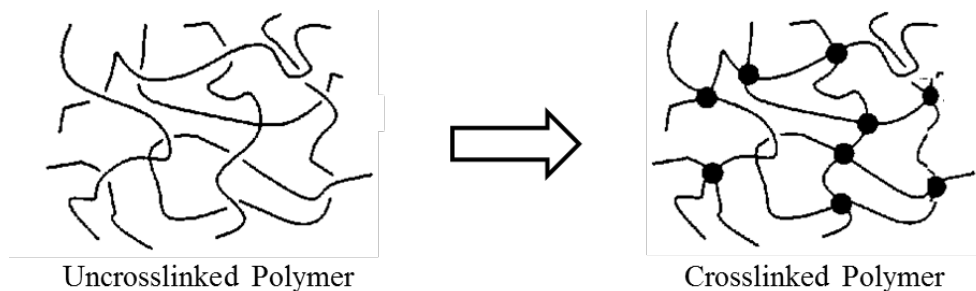


Figure 1.2: Polymer Crosslink Network¹

The cure deficiencies of PIB were overcome in 1940 with the invention of poly(isobutylene-*co*-isoprene) (IIR, Figure 1.1) by the Standard Oil Development Company.³ Known widely as butyl rubber, IIR is a random copolymer comprised of 1-2 mol% 2-methyl-1,3-butadiene (isoprene) and 98-99 mol% 2-methylprop-1-ene (isobutylene), where isoprene mers are incorporated randomly and predominately by 1,4-addition (Figure 1.1).⁴ The residual unsaturation provided by the isoprene mers is amenable to chemical modification, in particular vulcanization by sulfur curing formulations. This makes butyl rubber ideal for tire inner tube applications, which is the principal market for IIR in developing countries.

Although the small amount of isoprene within IIR facilitates sulfur vulcanization, it cures more slowly than diene-rich materials such as poly(butadiene) and poly(isoprene) that are used in tire sidewall and tread compounds. The inner liner of a tubeless tire must be cured at a similar rate to the other tire components, and IIR is not reactive enough for this application.⁵ To increase sulfur vulcanization rates, IIR is halogenated to yield brominated poly(isobutylene-*co*-isoprene) (BIIR, Figure 1.1). The heightened reactivity of the allylic bromide functionality within the halogenated

polymer toward nucleophilic displacement by sulfur provides vulcanization rates that are comparable to other tire components. As a result, about 85% of BIIR is sold to the tire inner liner market, with the balance used in pharmaceutical stoppers and other consumer goods.

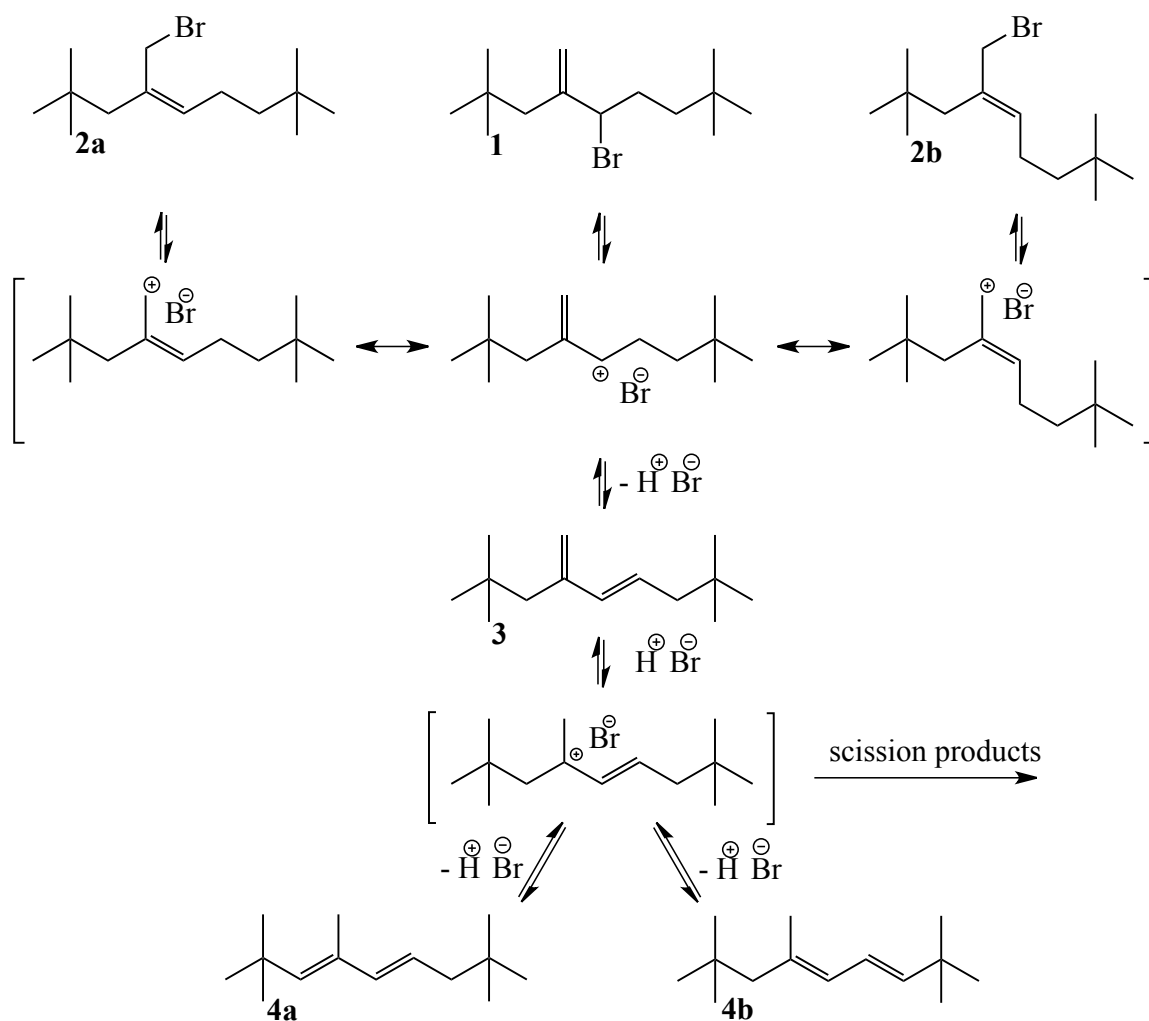
In 1989 a patent was issued for random copolymers comprised of 1-5 mol% 1-methyl-*para*-vinylbenzene (*para*-methylstyrene) and 95-99 mol% isobutylene.⁶ A lack of backbone unsaturation within poly(isobutylene-*co-para*-methylstyrene) (IMS, Figure 1.1) led to improved oxidative and thermal stability when compared to IIR. Air and moisture permeability were also comparable to IIR, due to the isobutylene-rich backbone.⁷ The initial intent of incorporating *para*-methylstyrene was the modification of physical properties, but there was little practical application owing to their inactivity toward conventional cure formulations. To facilitate crosslinking reactions, bromination of the *para*-methylstyrene functionality yields a brominated derivative of poly(isobutylene-*co-para*-methylstyrene) (BIMS, Figure 1.1), which contains a reactive benzylic bromide species. This functionality is reactive toward a number of conventional rubber crosslinking reactions, making it useful for applications similar to those of BIIR.

1.2 Chemical Modification of BIIR and BIMS

The allylic and benzylic halide functionality within BIIR and BIMS, respectively, is reactive toward a wide range of nucleophiles, making them attractive starting materials for the synthesis of functional isobutylene-rich elastomers. Undesirable complications can arise from the susceptibility of the allylic bromide within BIIR toward isomerization and hydrogen bromide elimination reactions.⁸ Scheme 1.1 illustrates well-established isomerization and elimination

reactions for brominated 2,2,4,8,8-pentamethyl-4-nonene (BPMN), a model compound⁹ for the allylic bromide functionality within BIIR.

Scheme 1.1: Isomerization and Elimination Reactions of BPMN



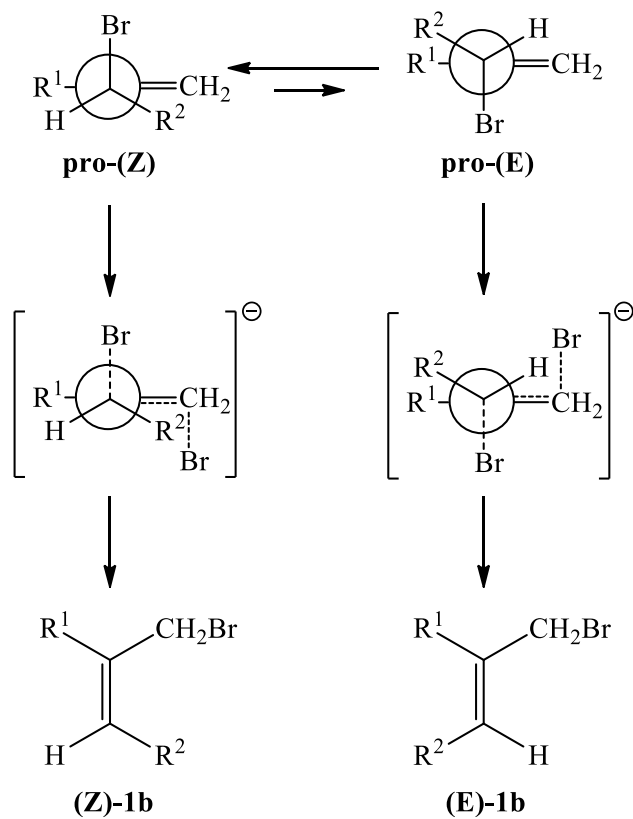
The exomethylene isomer (**1**, Exo-Br) is a kinetically favoured halogenation product that isomerizes to the thermodynamically more stable *E/Z-endo*-bromomethyl isomers (**2a**, **2b**) at

elevated temperatures. This rearrangement proceeds through an ionization/ion-pair collapse mechanism, which can be accompanied by allyl cation deprotonation to give an exo-conjugated diene (**3**). Acid-catalyzed isomerization of this functionality leads to other conjugated dienes, and may lead to molecular weight degradation through β -scission of cationic intermediates. To mitigate degradation, commercial grades of BIIR contain neutral acid scavengers such as epoxidized soybean oil, which removes HBr through bromohydrin formation. In contrast, BIMS is more thermally stable than BIIR and dehydrohalogenation reactions have not been reported.^{6, 10}

The Exo-Br (**1**) functionality within BIIR is also susceptible to nucleophilic rearrangement when exposed to tetra-N-alkylammonium bromide salts.¹¹ These isomerization reactions are highly selective for the *Z-endo*-bromomethyl (**2a**) isomer, which is caused by an abnormal nucleophilic substitution (S_N2') mechanism. The S_N2' mechanism has been postulated for a number of sterically hindered allylic halides, similar to BIIR, where bulky substituents direct the nucleophile to attack the allylic double bond, with the subsequent isomerization of the double bond and loss of the halide anion.¹² In cases where the nucleophilic bromide anion has a non-coordinating counterion, it has been observed that the reaction proceeds through an *anti* conformation of nucleophile and leaving group, in the transition state.¹³ Scheme 1.2 displays two conformations in butyl rubber that are able to undergo an S_N2' reaction through an *anti* conformation of nucleophile and leaving group. The reaction may proceed through one of two isomers (or their mirror images); the pro-(*Z*) conformer to produce the *Z-endo*-bromomethyl isomer (**2a**) or through the pro-(*E*) conformer to produce the *E-endo*-bromomethyl isomer (**2b**). Computational studies have been used to calculate the torsional energy profiles of the pro-(*Z*) and pro-(*E*) conformers and have shown non-bonding interactions between R¹ and R² in the pro-(*E*)

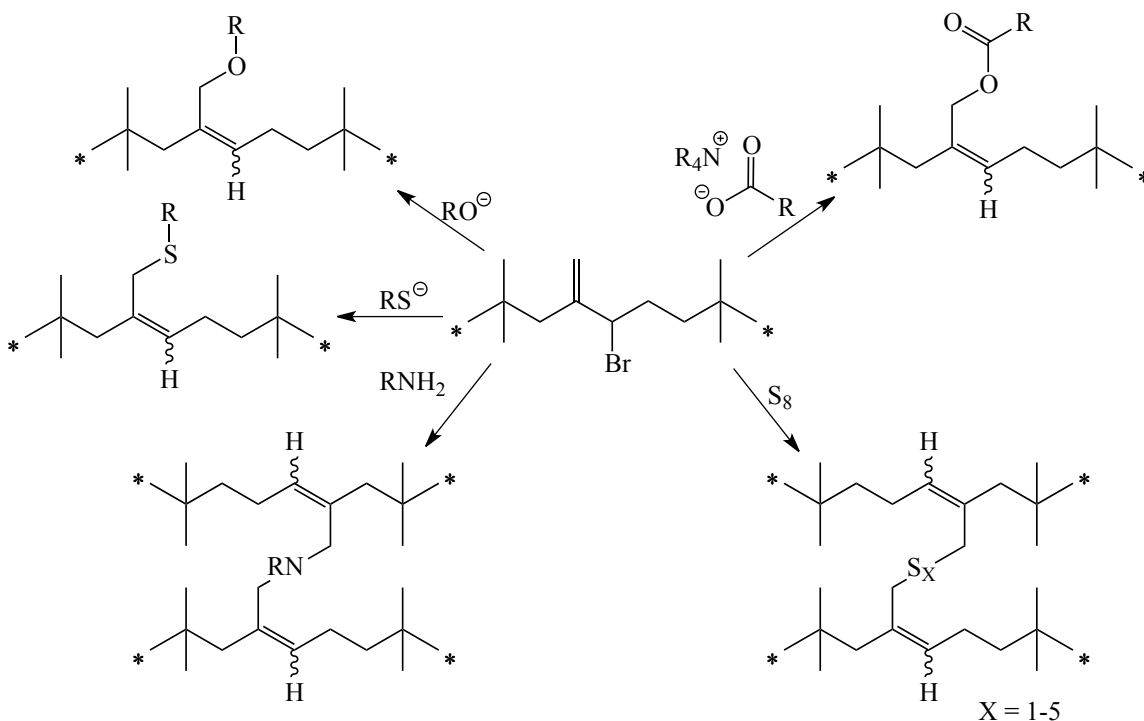
conformer make it less stable than the pro-(Z) conformer.¹⁴ Selectivity for the *Z-endo*-bromomethyl isomer (**2a**) is a consequence of the stability of the pro-(Z) conformer and the preference for the reaction to proceed through this lower energy transition state.

Scheme 1.2: S_N2' Rearrangement of Exo-Br Functionality in BPMN¹⁴



Halide displacement from BIIR and BIMS has been used to produce a wide range of functional isobutylene-based copolymers. Scheme 1.3 illustrates the versatility of the allylic bromide functionality in BIIR to produce sulfide, ether, ester, thio-ether and amine derivatives.

Scheme 1.3: Derivatization of the Allylic Bromide Functionality in BIIR



Sulfide (S_x) derivatives of BIIR are found in all tire inner liners making them industrially important reaction products. Sulfur can react with brominated pentamethylnonene (BPMN) to form dimers containing a single sulfur atom (monosulfide), two sulfur atoms (disulfide) or greater than two sulfur atoms (polysulfide).¹⁵ The sulfur-sulfur bonds in disulfide and polysulfide crosslinks are quite weak and they may break and reform under stress, providing good dynamic properties to sulfur-cured rubber articles.¹⁶ Sulfur-cured articles require toxic amidine bases and mercaptobenzthiazole disulfides to achieve desirable physical properties. These toxic compounds remain in the rubber article and may leach out over its lifetime.

Nucleophilic substitution by oxygen nucleophiles has been investigated for both BIIR and BIMS. The Williamson ether synthesis has been used in the synthesis of poly(ethylene oxide) and polybutadiene grafted BIIR.¹⁷ Another method of synthesizing functional derivatives of BIIR and BIMS is to utilize tetra-N-butylammonium carboxylate salts in nucleophilic substitution reactions.^{10, 18} Through this method, polyisoprene and polystyrene graft copolymers of BIMS have been synthesized. The grafting of polybutadiene and polyisoprene modifies polymer properties and allows these functional derivatives to be crosslinked by a wider range of crosslinking chemistry.

Bromide displacement by thiolate nucleophiles has been used to prepare thioether derivatives of BIIR that bear trialkoxysilane functionality.¹⁹ The latter can react with silanol groups on the surface of precipitated silica, thereby developing a covalent bond between polymer and filler. This type of coupling reaction is required for high surface energy fillers such as silica and clay, which are difficult to disperse in non-polar isobutylene-based elastomers. The nucleophilic substitution of BIIR by mercaptopropyltrimethoxysilane has been shown to provide the necessary compatibilization when silica is mixed with the elastomer, yielding well dispersed filled compounds with mechanical properties far superior to standard BIIR vulcanizates.

Nucleophilic substitution of BIIR by amines has also been studied.²⁰ Primary amines undergo multiple N-alkylations by allylic bromides and benzylic bromides to give crosslinked, thermoset derivatives of BIIR and BIMS. Secondary amines can also undergo N-alkylation to produce polymer-bound tertiary amines, but the reversibility of these reactions results in low overall

yields. N-alkylation of tertiary amines by BIIR and BIMS produce polymer-bound, quaternary ammonium bromide salts. It has been shown that these ion-containing polymers, or ionomers, have dynamic rheological properties similar to those of sulfur-cured rubber articles.¹⁶

1.3 Ionomer Derivatives of Isobutylene-rich Elastomers

Ionomers are polymers containing less than 15 mol% of ionic functionality that is distributed uniformly along a polymer backbone. Poor solvation of polymer-bound ions by a non-polar matrix can result in extensive aggregation to form multiplets that contain a small number (2-8) of ion pairs. If the material's ionic content is sufficient, multiplets may aggregate further to form clusters. Polymer chain mobility is restricted in the volume surrounding a multiplet, as illustrated in Figure 1.3 for poly(styrene-*co*-sodium acrylate), resulting in an extended rubbery plateau and, in some cases, a broadening of the glass transition temperature or appearance of a second glass transition temperature.²¹

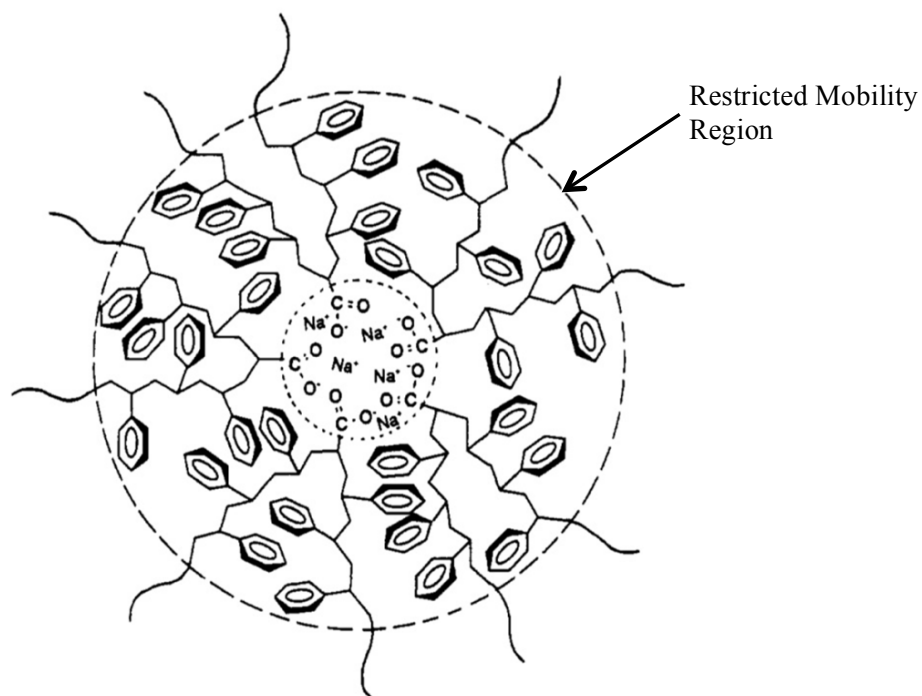


Figure 1.3: Restricted Mobility Region in a Poly(styrene-*co*-sodium acrylate) Ionomer²¹

The introduction of ion pairs to a non-polar elastomer has a great effect on its tensile properties, altering them to approach those of covalently crosslinked rubbers. The potential for ion-dipole interactions also improves adhesion to high energy surfaces (metals, glass, polar polymers), and can improve the dispersion of siliceous fillers during conventional rubber compounding operations.²² Ionomers bearing organic cations, such as phosphonium and ammonium functionality, have also attracted interest owing to their anti-microbial activity. Since the ionic functionality is polymer bound, anti-microbial activity is achieved without potential leaching problems associated with ionic liquid additives or metal nanoparticle technology.²³

Kennedy and coworkers²⁴ prepared the first isobutylene-based ionomers containing sulfonate functionality at both chain ends. In spite of their low molecular weight, these ionomers displayed an extended rubbery plateau with tensile strength approaching that of covalently crosslinked vulcanizates. However, as is commonplace for all elastomeric ionomers, the polymer network established by sulfonate group aggregation was labile, resulting in excessive stress relaxation and permanent set when the material was exposed to a static load. Therefore, the lability of ionic bonds requires crosslinking to provide suitable physical properties for engineering applications.

The Parent group has prepared several ionomer derivatives of BIIR through solvent-free nucleophilic substitution reactions with triphenylphosphine (PPh_3), tertiary amines (NR_3), and azoles such as N-butylimidazole (BuIm). These processes introduce allylic “onium” bromide functionality pendant to the polymer backbone (Figure 1.4) in a manner used for ionic liquid preparations,²⁵ although the conditions required to produce ionomers differ substantially from those used in small molecule systems.²⁶

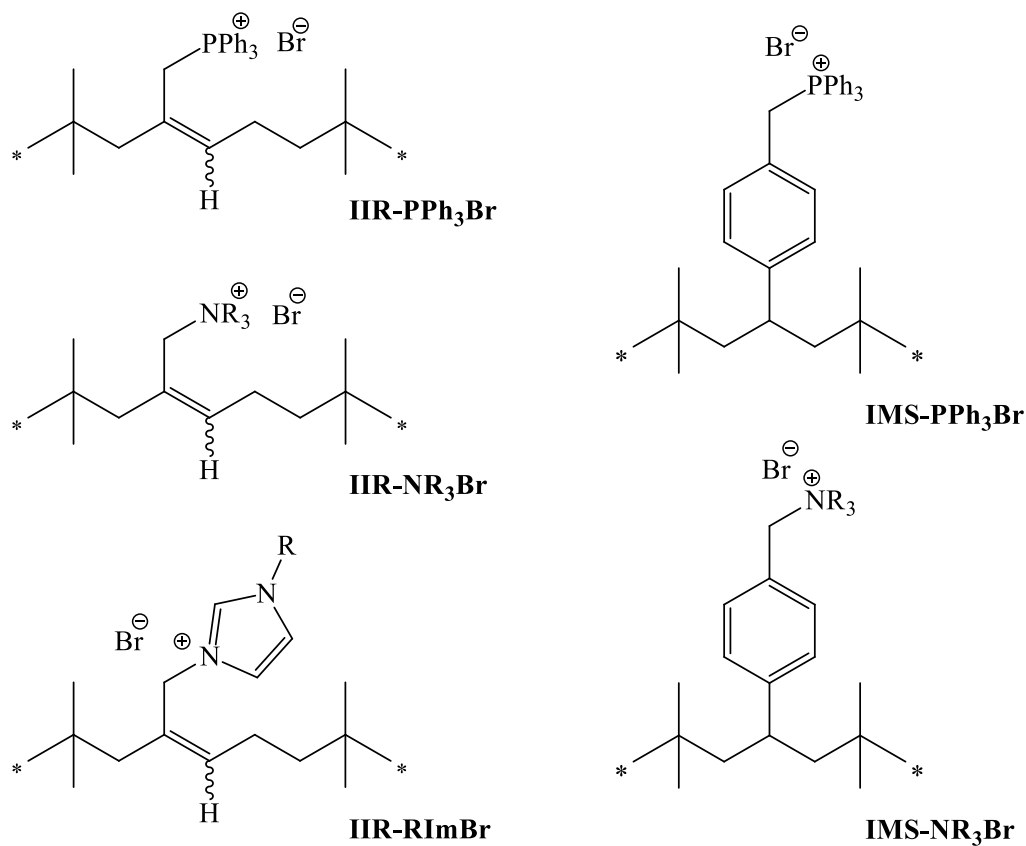


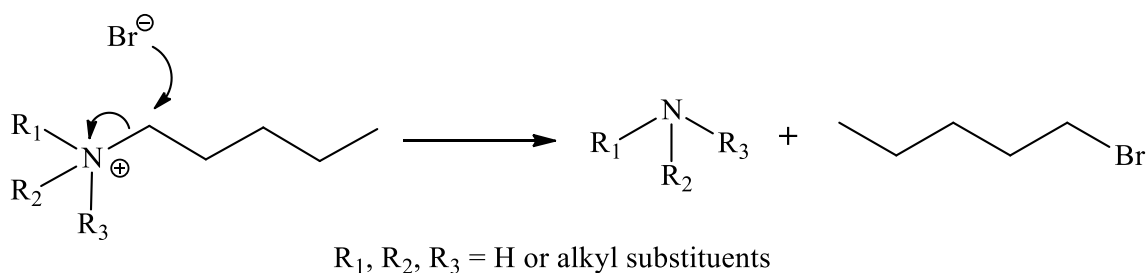
Figure 1.4: Ionomer Derivatives of BIIR and BIMS

Of these ionomer derivatives, IIR-PPH₃Br (Figure 1.4) has received the most attention owing to its ease of preparation and thermal stability. This material can be prepared under solvent-free conditions using conventional polymer processing equipment, and provides all of the aforementioned cationic ionomer properties.²⁷ A BIMS derivative, IMS-PPH₃Br (Figure 1.4), has also been produced, in tetrahydrofuran solution, where it was demonstrated that anion metathesis reactions can be used to alter the properties of these isobutylene-based ionomers.²⁸ One application of commercial interest concerns the mixing of isobutylene-rich elastomers with reinforcing fillers. Whereas it is difficult to disperse standard precipitated silicas within IIR, BIIR,

IMS or BIMS, the corresponding phosphonium bromide ionomer derivative provides the polymer-filler interactions required to disperse these materials with conventional mixing processes.²⁹ A shortcoming of IIR-PPh₃Br is its lack of residual allylic bromide functionality, which results in slow sulfur vulcanization rates. An ionomer that is capable of curing efficiently would have desirable dynamic properties and filler dispersion properties without a susceptibility to creep and stress relaxation.

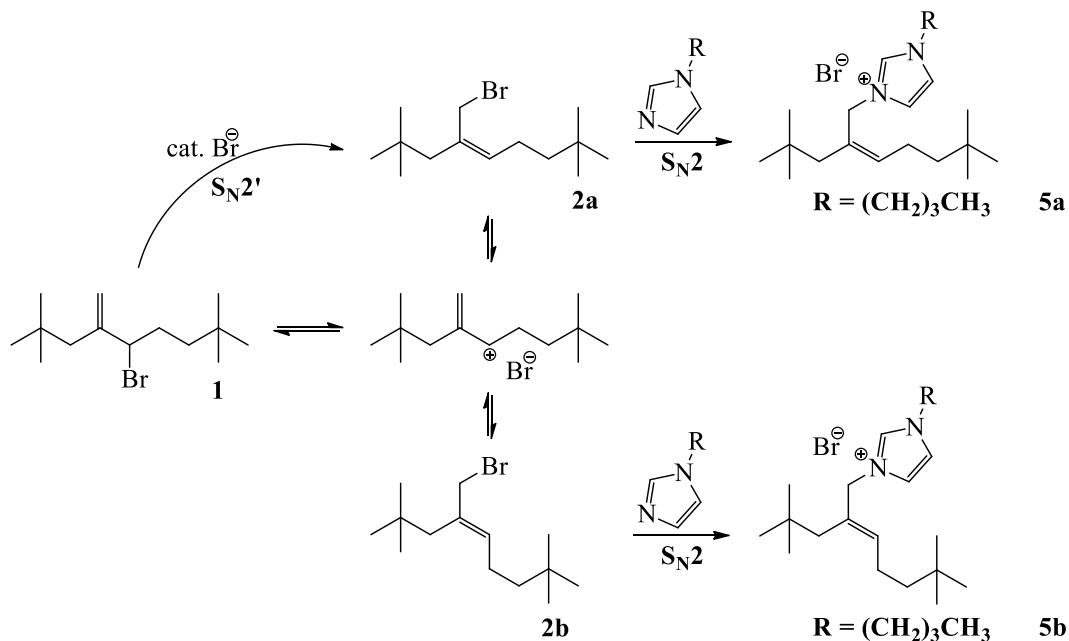
Tetra-N-alkylammonium bromide ionomers, IIR-NR₃Br and IMS-NR₃Br (Figure 1.4), have also been studied extensively, since amines with a variety of functionalities are commercially available.^{20, 30} Unfortunately, N-alkylation of tertiary amines by BIIR is reversible, requiring a large excess of amine to push allylic halide conversion to completion. This reversibility is attributed to a reverse Menshutkin reaction in which bromide displaces amine from the ionomer (Scheme 1.4).^{20, 31} In contrast to ammonium halide derivatives of BIIR, phosphonium and imidazolium halide derivatives of BIIR are relatively stable at the temperatures commonly encountered by elastomeric materials.^{27, 32}

Scheme 1.4: Reverse Menshutkin Reaction for a Tetra-N-Alkylammonium Bromide³¹



A wide variety of functional imidazoles are also commercially available, which makes them attractive nucleophiles for functionalization of BIIR and BIMS. N-alkylation of N-butylimidazole by BIIR to produce an isobutylene-based N-butylimidazolium bromide ionomer, IIR-BuImBr (Scheme 1.5), has been carried out under solvent-free conditions and in toluene solution.^{32, 33} In both cases, the rate limiting step seems to be the N-alkylation reaction, rather than isomerization of exomethylene allylic bromide to more reactive isomers. Solvent-free reactions of N-butylimidazole and isomerized BIIR have similar reaction rates to analogous reactions using an “as received” BIIR starting material. Analysis of the reaction products shows that only *E/Z-endo*-IIR-BuImBr (**5a**, **5b**) species form from the quaternization reaction; no exo-imidazolium bromide salt analogous to **1** was observed.

Scheme 1.5: Synthesis of an N-butylimidazolium Bromide Ionomer Derivative of BIIR³³



Imidazolium halides have received considerable attention in the ionic liquid field due to their versatile functionality and thermal stability. They are generally stable to about 200 °C,³⁴ and IIR-BuImBr did not undergo a reverse-Menschutkin reaction at or below 160 °C, unlike IIR-NR₃Br.³³ Additionally, heating a toluene solution of IIR-BuImBr and tetra-N-butylammonium acetate showed no exchange of nucleophiles after two hours. This robustness of IIR-BuImBr makes it suitable for processing at the temperatures used for rubber compounding and crosslinking.

The primary deficiency of the N-butylimidazolium bromide ionomer, shown in Scheme 1.5, is its susceptibility to creep and stress relaxation. Crosslinking of the ionomer is required, but as stated previously, the conversion of allylic or benzylic bromide to polymer-bound ion-pairs consumes the reactive functionality needed for efficient sulfur vulcanization. Peroxide-initiated curing is an attractive alternative, if an isobutylene-rich ionomer bears functionality that engages in free radical crosslinking.

1.4 Peroxide Curing Derivatives of Isobutylene-based Elastomers

The rubber industry uses two main classes of cross-linking chemistry; sulfur-based cure formulations and peroxide-based cure formulations.³⁵ Sulfur-based formulations typically provide superior dynamic properties such as flex fatigue, owing to the labile nature of their polysulfide crosslinks. Where cross-link stability is paramount, peroxide cures are preferred owing to the strength of carbon-carbon bonds generated by this technology. Whereas a sulfur-cured article may experience some irreversible compression when subjected to a sustained load, a peroxide-cured material is less susceptible to compression set and stress relaxation.¹⁶ Peroxide formulations are also desired where curative leaching is an important design variable, since their

cure byproducts are simple ketones and alcohols. Sulfur-based formulations, on the other hand, typically contain aryl guanidine bases and mercaptobenzthiazole disulfides that may be harmful to human health.

The chemistry that underlies peroxide-only cures is relatively well understood. Figure 1.5 is an illustration of a stoichiometric free radical cross-linking process that is initiated by an organic peroxide (ROOR, Figure 1.5), where in this case, “P” represents a polymer chain (rather than a phosphorus atom as in PPh₃, used previously). Thermolysis of the weak oxygen-oxygen bond is a relatively slow, first-order decomposition process that yields reactive alkoxy radical intermediates. Since the rate of peroxide breakdown is strongly temperature dependent, initiators are chosen on the basis of their half-life at the desired curing temperature. Dicumyl peroxide has a half-life of approximately 5 min at 160 °C, and is commonly used as an initiator for rubber crosslinking.³⁶

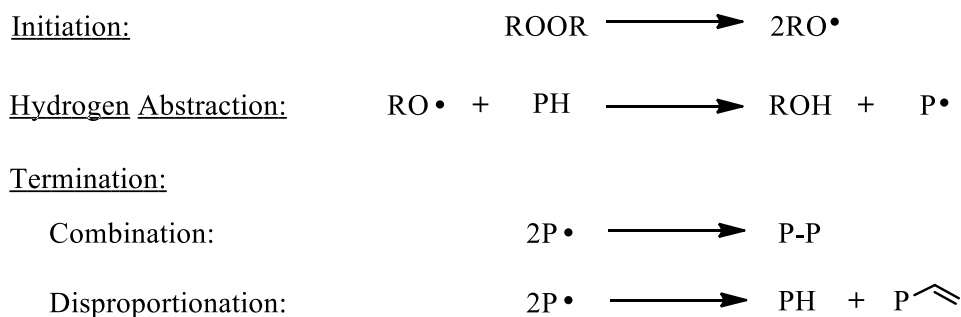
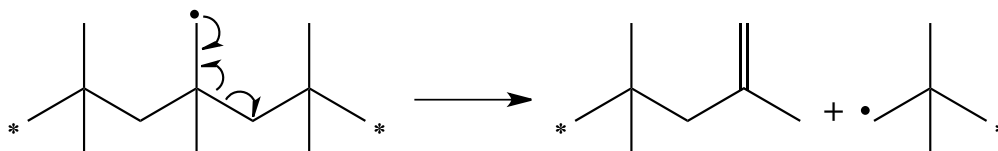


Figure 1.5: A Simplified Mechanism for Peroxide-only Crosslinking Formulations³⁵

Polymer cross-linking involves the production of macroradicals ($P\bullet$, Figure 1.5) through hydrogen atom abstraction from the polymer backbone (PH, Figure 1.5) by initiator-derived alkoxy radicals. Radical termination is extremely rapid, with combination generating a cross-link, and disproportionation having no immediate effect on polymer molecular weight. This hydrogen abstraction and radical termination process is not a chain reaction, but an open reaction sequence. As such, the number of crosslinks cannot exceed the amount of initiator used in the formulation. In practice, these stoichiometric cures achieve less than quantitative yields, given the effects of radical disproportionation as well as inefficiencies in producing macroradicals by hydrogen transfer.³⁷ The efficiency of a peroxide crosslinking reaction can be determined by calculation of the peroxide yield. Peroxide yield is defined as the moles of reactive functionality consumed per mole of peroxide used for the crosslinking reaction. This method considers all free radical species formed, even those that do not contribute to crosslinking reactions, establishing a lower limit for potential chain character of the reaction.

Peroxide cures are effective for most saturated elastomers such as hydrogenated nitrile-butadiene rubber and ethylene-propylene copolymers. However, they do not cure isobutylene-rich elastomers, due to β -scission of polymer macroradicals, as shown in Scheme 1.6.³⁸ This unimolecular fragmentation lowers the material's molecular weight to a greater extent than radical combination increases molecular weight. As a result, polyisobutylene degrades when treated with peroxides at conventional cure temperatures. The 1-2 mole % of unsaturation within IIR lessens the extent of polymer degradation, but does not support a free radical cure.³⁹ As such, commercial grades of IIR are only cured by sulfur-based formulations.

Scheme 1.6: β -Scission of Primary Polyisobutylene Macroradicals



1.4.1 Macromonomer Derivatives of Isobutylene-based Elastomers

Oxley and Wilson prepared the first peroxide-curable isobutylene-rich elastomer by polymerization of isobutylene, isoprene and divinylbenzene (Figure 1.6).⁴⁰ The divinylbenzene monomer provides reactive unsaturation that is able to crosslink when heated in the presence of peroxide, rather than the degradation observed for other isobutylene-rich elastomers. Similar results were observed for copolymers of isobutylene and divinylbenzene. These materials, called macromonomers, cure through free radical oligomerization of pendant vinyl functionality, as opposed to the H-atom abstraction + radical combination process described above. Since the formation of polymer backbone macroradicals can be avoided in these cure systems, isobutylene-rich macromonomers can be crosslinked to high extent using relatively small amounts of peroxide. Unfortunately, the cationic polymerization of isobutylene with divinylbenzene gives a polymer that is already significantly crosslinked. The gel contents of these materials can reach 85%, which makes them difficult to mix with other compound ingredients. Polysar Rubber adapted this technology to produce a terpolymer with approximately 1.3 mol% of crosslinked divinylbenzene functionality, known by the tradename XL-10,000.⁴¹ The lowered gel content

was still enough to render the polymer insoluble in solvents and present difficulties for extrusion and other processing operations.

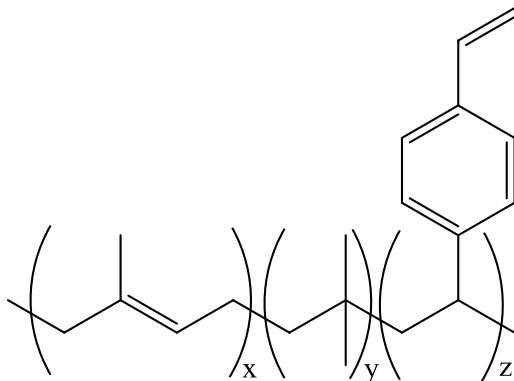
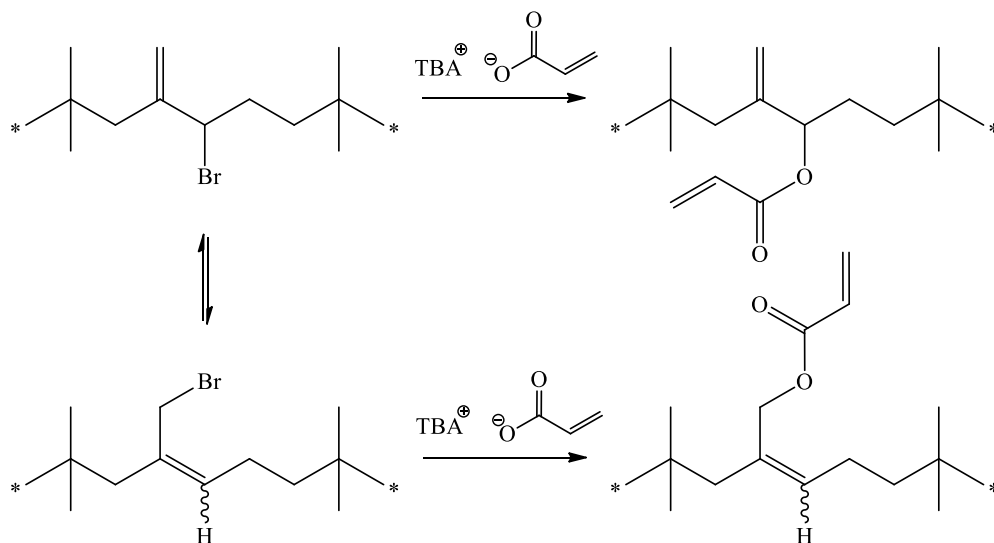


Figure 1.6: Structure of an Isobutylene, Isoprene and Divinylbenzene Terpolymer

Gel-free macromonomers can be prepared by exploiting the allylic and benzylic bromide functionalities in BIIR and BIMS, respectively. Nucleophilic substitution to introduce pendant acrylate functionality has been investigated for both polymers.^{42, 43} Scheme 1.7 illustrates the use of tetra-N-butylammonium (TBA) acrylate to produce the desired macromonomer derivatives of BIIR. These materials are highly reactive, and crosslinking can occur at high temperature even in the absence of a radical initiator.⁴² As a result of this propensity to oligomerize, the storage stability of these macromonomers at room temperature was insufficient.

Scheme 1.7: Synthesis of Acrylate Derivatives of BIIR



There are a number of commercially available vinylazoles and vinylazines that could be used to produce peroxide-curable ionomer derivatives of BIIR or BIMS. A comparison of the N-alkylation of 1-methylimidazole, pyridine, oxazole and thiazole by methyl iodide has shown that imidazoles have the fastest substitution rates among these heterocycles.⁴⁴ Fast N-alkylation rates reduce reaction times and may prevent undesired gel formation during nucleophilic substitution. N-vinylimidazole is a commercially available monomer that is able to undergo N-alkylation to produce an ionomer derivative that bears a reactive vinyl group, which may support peroxide crosslinking. The polymerization of N-vinylimidazolium halides is quite slow when compared to other vinyl azoles or azines.⁴⁵ This sluggishness towards polymerization may be beneficial in a BIIR or BIMS derivative as it may impart high temperature stability and storage stability that was not observed in previous macromonomer derivatives of BIIR and BIMS.

1.5 Research Objectives

The objectives of this work included the preparation of N-vinylimidazolium bromide ionomer derivatives of BIIR and BIMS, the assessment of their peroxide-initiated cure dynamics, and the evaluation of physical properties. These goals were approached through the following steps.

1. Study of the N-alkylation dynamics of N-vinylimidazole with BIIR and BIMS.
2. Investigation of the thermal stability and peroxide crosslinking reactions of these new materials.
3. Assessment of the physical properties of the vulcanized materials, including tensile properties, relaxation/creep and viscoelasticity.
4. Determine the ability of these ionomers to disperse conventional rubber fillers such as carbon black and precipitated silica.

1.6 References

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Chapter 2: The Synthesis and Physical Properties of an N-vinylimidazolium Bromide Derivative of BIIR

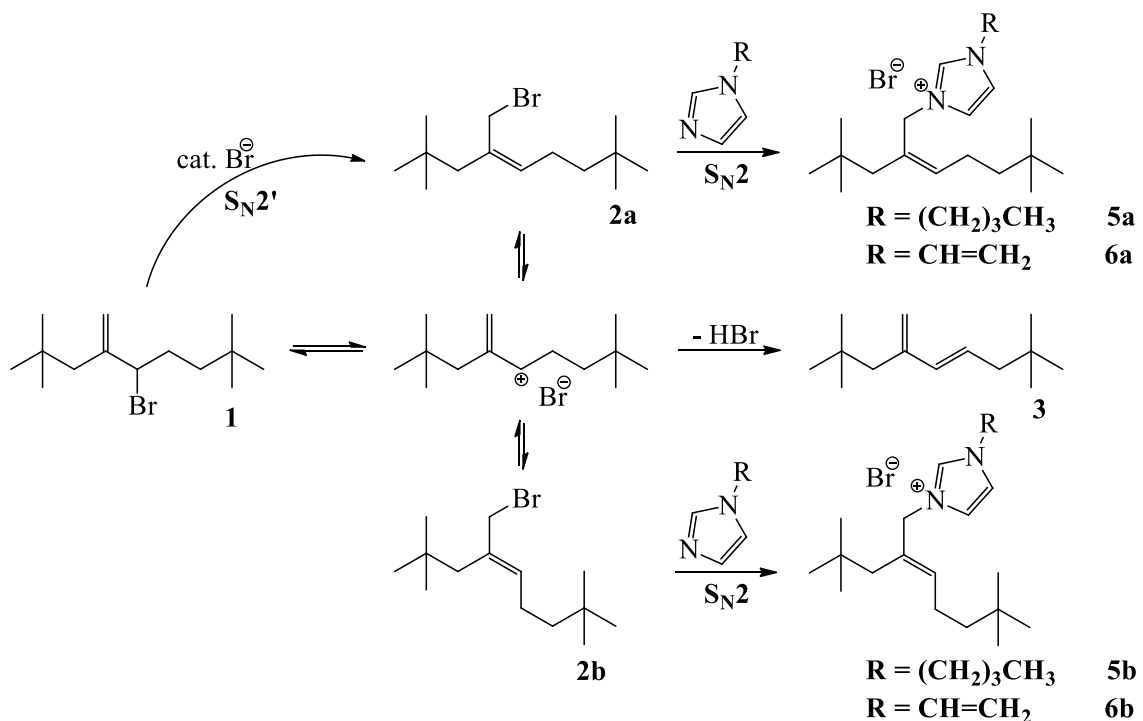
2.1 Introduction

Ionomers are polymers containing less than 15 mol% of ionic functionality that is distributed uniformly along a polymer backbone. Poor solvation of polymer-bound ions by a non-polar matrix can result in extensive ion-pair aggregation.¹ The physical properties of ionomers approach those of covalently crosslinked elastomers as a result of this ion-pair aggregation. As with any uncrosslinked elastomer, ionomers are susceptible to creep and stress relaxation, which creates a need for thermoset ionomer chemistry.

Previous research has focused on triphenylphosphonium bromide (IIR-PPh₃Br) and tetra-N-alkylammonium bromide (IIR-NR₃Br) ionomeric derivatives of butyl rubber but these materials are not suitable for thermoset ionomer chemistry.² Most commercially available phosphines are air-sensitive, and there are challenges associated with preparing functional phosphines, which limits the practicality of P-alkylation by BIIR.³ N-alkylation of tertiary amines by BIIR is reversible, which is disadvantageous as it requires excess amine to reach full allylic halide conversion, which in turn causes plasticization.⁴ These cationic ionomers did, however, exhibit a number of desirable properties including anti-microbial activity⁵ and the ability to disperse siliceous fillers⁶, yet they are not practical for generating ionomer thermosets.

Parent *et al.* have shown that functional imidazoles can be used in the synthesis of ionomers and ionomer thermosets.⁷ N-alkylation of N-butylimidazole (BuIm) by BIIR is a facile method of producing ionomers with the potential to contain reactive functionalities besides an alkyl substituent (Scheme 2.1). Practical compounding methods have also been used to produce ionomer thermoset articles by mixing difunctional imidazole nucleophiles with BIIR. Crosslinking occurs by subsequent N-alkylation of the imidazole species after compounding. The advantage of N-alkylation of a functional imidazole species, such as N-vinylimidazole (Scheme 2.1), is that the N-vinylimidazolium bromide salts can be used to achieve filler dispersion during compounding, unlike the difunctional imidazole species, where the ionomer is produced after the mixing process.

Scheme 2.1: Synthesis of Functional Imidazolium Bromide Derivatives of BIIR



2.2 Experimental

Materials. N-vinylimidazole (VIm, 99+%), N-butylimidazole (BuIm, 98%), acrylic acid (anhydrous, 99%), tetra-N-butylammonium hydroxide (TBAOH, 1.0 M in methanol), tetra-N-butylammonium bromide (TBAB, 99%), tetra-N-butylammonium acetate (TBAAc, 97%), chloroform-*d* (99.8%D), methanol-*d*₄ (99.8%D), toluene-*d*₆ (99.6%D) and dicumyl peroxide (DCP, 98%) were used, as received, from Sigma Aldrich (Oakville, Ontario). BIIR (BB 2030, $M_n = 400\,000$ g/mol, polydispersity = 1.5, 0.15 mmol allylic bromide functionality/g BIIR) was used as supplied by LANXESS Inc. (Sarnia, Ontario). Brominated 2,2,4,8,8-pentamethyl-4-nonene (BPMN) was prepared as previously described.⁸

Synthesis of (E,Z)-3-(6,6-dimethyl-2-neopentylhept-2-en-1-yl)-1-vinyl-1-imidazol-3-ium bromide. BPMN (18 mg, 0.08 mmol) was heated to 100 °C in toluene-*d*₈ (0.80 mL) for 48 h to isomerize from the Exo-Br (**1**) to a 60:40 ratio of **2a** : **2b**. The resulting solution was then charged with VIm (7.5 mg, 0.08 mmol, 1 eq.) and heated for 50 h, at 100 °C. A viscous brown liquid separated from the toluene phase and the toluene phase was decanted out of the NMR tube. Residual VIm and BPMN was removed by washing with toluene-*d*₈. Toluene-*d*₈ was removed by Kugelrohr distillation (80 Pa, 60 °C) to yield a viscous, brown liquid. High resolution MS analysis; required for C₁₉H₃₃N₂⁺ *m/e* 289.2640; found *m/e* 289.2644. ¹H NMR (CDCl₃): δ 7.67 (s, 1H, -N-**CH**=CH-N⁺-), δ 7.56 (dd, 1H, -N-**CH**=CH₂), δ 5.94 (dd, 1H, N-CH=CH-**H**_{trans}), δ 5.42 (dd, 1H, N-CH=CH-**H**_{cis}), δ 0.80 – 1.0 (4 · s, 18H, 2 · (CH₃)₃), found for the Z-isomer: δ 11.18 (s, 1H, -N⁺-**CH**-N-), δ 7.16 (s, 1H, -N⁺-**CH**=CH-N-), δ 5.72 (t, 1H, CH₂-C=**CH**-CH₂), δ 4.99 (s, 2H, -C-**CH**₂-N⁺), δ 2.13 (q, 2H, C=CH-**CH**₂-CH₂-), δ 1.83 (s, 2H, (CH₃)₃-C-CH₂-C=), δ 1.27 (t, 2H, =CH-CH₂-CH₂-C-(CH₃)₃), found for the E-isomer: δ 11.09 (s, 1H, -N⁺-**CH**-N-), δ 7.22

(s, 1H, $-\text{N}^+-\text{CH}=\text{CH}-\text{N}-$), δ 5.719 (t, 1H, $\text{CH}_2-\text{C}=\text{CH}-\text{CH}_2$), δ 4.91 (s, 2H, $-\text{C}-\text{CH}_2-\text{N}^+$) δ 2.06 (q, 2H, $\text{C}=\text{CH}-\text{CH}_2-\text{CH}_2-$), δ 1.91 (s, 2H, $(\text{CH}_3)_3-\text{C}-\text{CH}_2-\text{C}=\text{C}$), δ 1.23 (t, 2H, $=\text{CH}-\text{CH}_2-\text{CH}_2-\text{C}-(\text{CH}_3)_3$). Peak assignments were confirmed with 2D ^1H NMR.

Synthesis of IIR-VImBr. BIIR (20 g, 3.0 mmol allylic bromide) was dissolved in toluene (100 mL, 10 wt%) and heated to 100 ± 2 °C. VIm (1.69 g, 18.0 mmol, 6 eq.) was then added to the solution and the mixture was allowed to react for 50 h. Aliquots (~0.5 mL) withdrawn at intervals were precipitated from excess acetone to isolate the polymeric reaction product, which was dried under vacuum and characterized by ^1H NMR spectroscopy. The N-alkylation product was obtained by precipitation in excess acetone and purified by dissolution/precipitation using tetrahydrofuran/acetone and dried *in vacuo*. IIR-VImBr was produced in 75% yield corresponding to an ion content of 0.11 mmol/g. The degree of N-alkylation was quantified by the integration of normalized proton ^1H NMR spectra to an estimated accuracy of ± 5 %. IIR-VImBr materials for tensile testing were scaled up to a 40.0 g batch, prepared from BIIR. ^1H NMR ($\text{CDCl}_3 + 5$ wt% CD_3OD) for IIR-VImBr: δ 11.53 (s, 1H, $-\text{N}^+-\text{CH}-\text{N}-$), δ 7.61 (s, 1H, $-\text{N}^+-\text{CH}=\text{CH}-\text{N}-$), δ 7.42 (dd, 1H, $-\text{N}-\text{CH}=\text{CH}_2$), δ 5.80 (dd, 1H, $\text{N}-\text{CH}=\text{CH}-\text{H}_{\text{trans}}$), δ 5.41 (dd, 1H, $\text{N}-\text{CH}=\text{CH}-\text{H}_{\text{cis}}$), found for the Z-isomer: δ 7.16 (s, 1H, Z, $-\text{N}^+-\text{CH}=\text{CH}-\text{N}-$), δ 5.69 (t, 1H, Z, $\text{CH}_2-\text{C}=\text{CH}-\text{CH}_2$), δ 4.91 (s, 2H, $-\text{C}-\text{CH}_2-\text{N}^+$), found for the E-isomer: δ 7.20 (s, 1H, E, $-\text{N}^+-\text{CH}=\text{CH}-\text{N}-$), δ 5.68 (t, 1H, E, $\text{CH}_2-\text{C}=\text{CH}-\text{CH}_2$), δ 4.84 (s, 2H, E, $-\text{C}-\text{CH}_2-\text{N}^+$). ^1H NMR for conjugated dienes: δ 5.98 (d, 1H, exo-diene), δ 5.92 (d, 1H, endo-diene). ^1H NMR for residual isoprene mer: δ 5.04 (t, 1H, $\text{CH}_3-\text{C}=\text{CH}-\text{CH}_2-$).

Synthesis of IIR-BuImBr. BIIR (20 g, 3.0 mmol allylic bromide) was dissolved in toluene (100 mL, 10 wt%) and heated to 100 ± 2 °C. BuIm (2.24 g, 18.0 mmol, 6 eq.) was then added to the solution and the mixture was allowed to react for 16 h. The N-alkylation product was obtained by precipitation in excess acetone and purified by dissolution/precipitation using tetrahydrofuran/acetone and dried *in vacuo*. IIR-BuImBr was produced in a 90% yield corresponding to an ion content of 0.135 mmol/g. The degree of N-alkylation was quantified by the integration of normalized proton ^1H NMR spectra to an estimated accuracy of ± 5 %. This procedure followed the work by Parent *et al.*⁷ IIR-BuImBr materials for tensile testing were scaled up to a 40.0 g batch, prepared from as-received BIIR. ^1H NMR ($\text{CDCl}_3 + 5$ wt% CD_3OD) for IIR-BuImBr: δ 4.89 (s, 2H, $=\text{C}-\text{CH}_2-\text{N}^+-$, Z-isomer), δ 4.82 (s, 2H, $=\text{C}-\text{CH}_2-\text{N}^+-$, E-isomer), δ 4.35 (t, 2H, $\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$). This ^1H NMR spectrum was consistent with previous work by Parent *et al.*⁷

Preparation of Tetra-N-butylammonium Acrylate. Acrylic acid (0.29, 4.0 mmol) was mixed with TBAOH (4 mL, 1.0 M in MeOH, 4 mmol) and stirred for 30 min at room temperature. Methanol was removed by Kugelrohr distillation at room temperature and 80 Pa to yield white crystals. This procedure followed work by Xiao *et al.*⁹

Preparation of IIR-Acrylate. BIIR (20 g, 3.0 mmol allylic bromide) was dissolved in toluene (200 mL, 10 wt%) and heated to 85 ± 2 °C. Tetra-N-butylammonium bromide (0.48 g, 0.5 mmol, 0.5 eq.) was added to the solution and the mixture was isomerized from **1** to **2a/2b** for 1 h. Tetra-N-butylammonium acrylate (1.03g , 3.3 mmol, 1.1 eq.) was added to the solution and allowed to

react for 2 hours to ensure allylic bromide conversion. The esterification product was obtained by precipitation in excess acetone and purified by dissolution/precipitation using tetrahydrofuran/acetone and dried *in vacuo*. IIR-Acrylate was produced in 100% yield corresponding to an acrylate content of 0.15 mmol/g. The degree of esterification was quantified by the integration of normalized proton ^1H NMR spectra to an estimated accuracy of $\pm 5\%$. This procedure followed work by Xiao *et al.*⁹ IIR-Acrylate materials for tensile testing were scaled up to a 40.0 g batch, prepared from as-received BIIR. ^1H NMR (CDCl_3) for IIR-Acrylate: δ 6.41 (d, 1H, $-\text{O}-\text{C}(=\text{O})-\text{CH}=\text{CH}-\mathbf{H}_{\text{trans}}$), δ 6.15 (m, 1H, $-\text{O}-\text{C}(=\text{O})-\mathbf{CH}=\text{CH}_2$), δ 5.82 (d, 1H, $-\text{O}-\text{C}(=\text{O})-\text{CH}=\text{CH}-\mathbf{H}_{\text{cis}}$), δ 4.68 (s, 2H, $=\text{C}-\mathbf{CH}_2-\text{O}-\text{C}(=\text{O})-$, *Z*-ester), δ 4.61 (s, 2H, $=\text{C}-\mathbf{CH}_2-\text{O}-\text{C}(=\text{O})-$, *E*-ester). ^1H NMR for residual isoprene: δ 5.07 (t, 1H, $\text{CH}_3-\text{C}=\text{CH}-\text{CH}_2$). This ^1H NMR spectrum was consistent with previous work by Xiao *et al.*⁹

Preparation of IIR-Acetate. BIIR (20 g, 3.0 mmol allylic bromide) and TBAB (0.48 g, 1.5 mmol, 0.5 eq.) were dissolved in toluene (200 mL, 10 wt%) and heated to $85 \pm 2\text{ }^\circ\text{C}$ for 1 h to isomerize from **1** to a ratio of **2a:2b**. TBAAc (1.13 g, 3.75 mmol, 1.25 eq.) was added to the solution and allowed to react for 2 h. The esterification product was obtained by precipitation in excess acetone and purified by dissolution/precipitation using tetrahydrofuran/acetone and dried *in vacuo*. IIR-Acetate was produced in 100% yield corresponding to an acetate content of 0.15 mmol/g. The degree of esterification was quantified by the integration of normalized proton ^1H NMR spectra to an estimated accuracy of $\pm 5\%$. This procedure followed work by Parent *et al.*¹⁰ ^1H NMR (CDCl_3) for IIR-Acetate: δ 5.18 (t, 1H, $=\text{C}-\mathbf{CH}-\text{O}-\text{C}(=\text{O})-\text{CH}_3$, Exo-ester), δ 4.58 (t, 2H, $=\mathbf{CH}_2-\text{O}-\text{C}(=\text{O})-\text{CH}_3$, *Z*-ester), δ 4.51 (t, 2H, $=\mathbf{CH}_2-\text{O}-\text{C}(=\text{O})-\text{CH}_3$, *E*-ester). ^1H NMR for conjugated dienes: δ 6.01 (d, 1H, exo-diene), 5.95 (d, 1H, endo-diene). ^1H NMR for residual

isoprene: δ 5.07 (t, 1H, CH₃-C=CH-CH₂). This ¹H NMR spectrum was consistent with previous work by Parent *et al.*¹¹

Preparation of Cured Macrosheets. A 40.0 g batch of dried elastomer was coated with the required amount of a solution of DCP in acetone and allowed to dry before being passed through a two roll mill ten times. A 5.0 g sample of the mixed compound was cured in the rheometer cavity at 160 °C, at a 3° oscillation arc and a frequency of 1 Hz to monitor cure dynamics. The remaining 33.0 g of the mixture was sheeted with a two-roll mill and compression molded at 160 °C and 20 MPa for 25 min ($5t_{1/2}$ for DCP³⁶).¹² The sheeted products had a thickness of 2.00 ± 0.05 mm.

Preparation of Cured Cylinders for Compression Set. The remaining 2.0 g of the 40.0 g batch were placed inside a cylindrical mold with a diameter of 14.0 mm and a height of 12.5 mm. The samples were cured at 160 °C for 25 min. The final cylinders had a diameter of 14 ± 0.1 mm and a height of 12.5 ± 0.2 mm.

Analysis. NMR characterization was done on a Bruker AM600 instrument and a Bruker AM500 instrument with chemical shifts (δ) reported relative to tetramethylsilane in ppm. A Waters/Micromass GC-T TOF mass spectrometer operating in electron impact mode acquired high-resolution mass spectrometry data

Rheological characterization was carried out in an oscillatory rheometer (Advanced Polymer Analyzer 2000, Alpha Technologies) operating in a parallel plate configuration. A 5.0 g sample of the uncured material was coated with the required amount of DCP in an acetone solution and allowed to dry before being passed through a two roll mill ten times. The mixed compound was cured in the rheometer cavity at 160 °C for 60 min, at a 3° oscillation arc and a frequency of 1 Hz. Stress relaxation measurements were conducted at 100 °C with a strain of 2° for 5 min. Temperature sweeps were conducted from 100 °C to 200 °C at a frequency of 1 Hz and a 3° oscillation arc.

Tensile strength data were acquired using an INSTRON Series 3360 universal testing instrument, operating at a crosshead speed of 500 mm/min at 23 ± 1 °C.¹³ Young's modulus was found by calculating the slope of the stress (MPa) vs. strain (mm/mm) curve from 0 mm to 0.2 mm of extension. Dog bones were cut from the specimen cutter described in ASTM D4482.¹⁴ Five replicate measurements were made for each sample to test the precision of the compounding and physical testing procedures.

Compression set measurements were carried out using a pneumatic press. Sample height was measured and samples, as well as stainless steel spacers, were placed on a stainless steel plate inside the press. The spacer height was 6.44 mm, corresponding to an applied strain of approximately 45 %. The apparatus was compressed with 3.5 MPa and left for 22 h. After 22 h, the samples were removed and rest for 0.5 h before the final height of the cylinders was measured. This procedure was adapted from ASTM D395 – 03 (2008).¹⁵

2.3 Results and Discussion

2.3.1 Synthesis and Peroxide Crosslinking of IIR-VImBr

Characterization of the reaction products of N-vinylimidazole (VIm) and BIIR is complicated by low allylic bromide concentrations in BIIR and the inability to isolate separate products. Brominated 2,2,4,8,8-pentamethyl-4-nonene (BPMN) has been used previously as a model of the reactive functionality of BIIR, thereby assisting with the characterization of BIIR derivatives.^{4, 8} N-alkylation of VIm by BPMN yields (*E,Z*)-3-(6,6-dimethyl-2-neopentylhept-2-en-1-yl)-1-vinyl-1-imidazol-3-ium bromide and no exomethylene isomer, analogous to **1**, was observed, as is consistent with previously prepared ionomer products.^{2, 7} There is excellent chemical shift agreement between IIR-VImBr and its model compound, shown in Figure 2.1. It has been shown that the addition of deuterated methanol to an ionomer solution in chloroform will sharpen peaks in the proton NMR by extending T₂ relaxation times.² The presence of three vinyl protons (**e**, **f**, **g**), in Figure 2.1, indicates that the vinyl functionality is stable to prolonged heating.

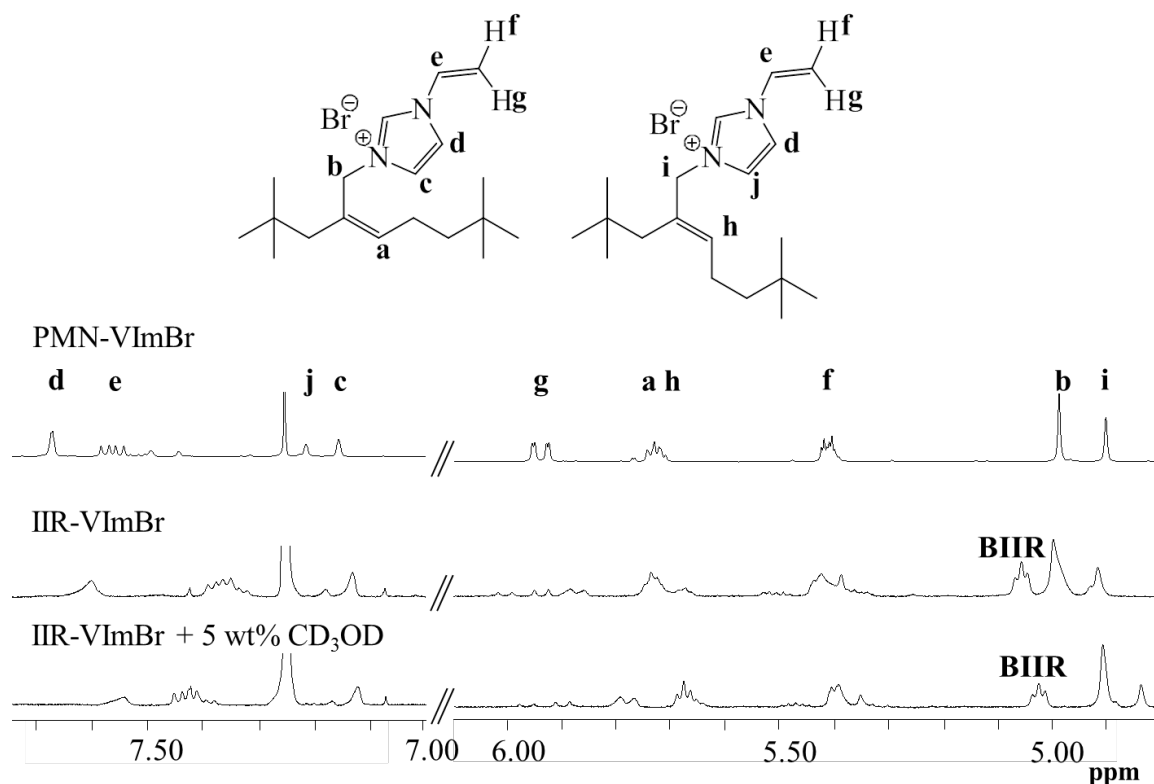


Figure 2.1: ¹H NMR Spectra of IIR-VImBr and its Model Compound

The N-alkylation of VIm by BIIR was carried out in a toluene solution at 100 °C. Initially, BIIR contained a 95:0:5 ratio of **1:2a:2b**, which was allowed to thermally isomerize while reacting with N-vinylimidazole, as shown in Figure 2.2. Similar to the N-alkylation of tertiary amines⁴ and N-butylimidazole⁷, N-alkylation of N-vinylimidazole is sensitive to nucleophile concentration and six molar equivalents of the nucleophile relative to the allylic halide functionality in solution were used to accelerate reaction rates. Allylic bromide conversion was complete after 50 hours, resulting in 0.11 mmol/g *E/Z*-N-vinylimidazolium bromide functionality with the remainder comprised of conjugated dienes (**3**, **4a**, **4b**), determined from ¹H NMR measurements. The distribution of ion-pairs along the polymer backbone is expected to be

random, since the allylic bromide functionality is randomly distributed. This N-alkylation reaction is much slower than the N-alkylation of N-butylimidazole (BuIm) by BIIR, which reaches full conversion in 6 h at the same conditions.⁷

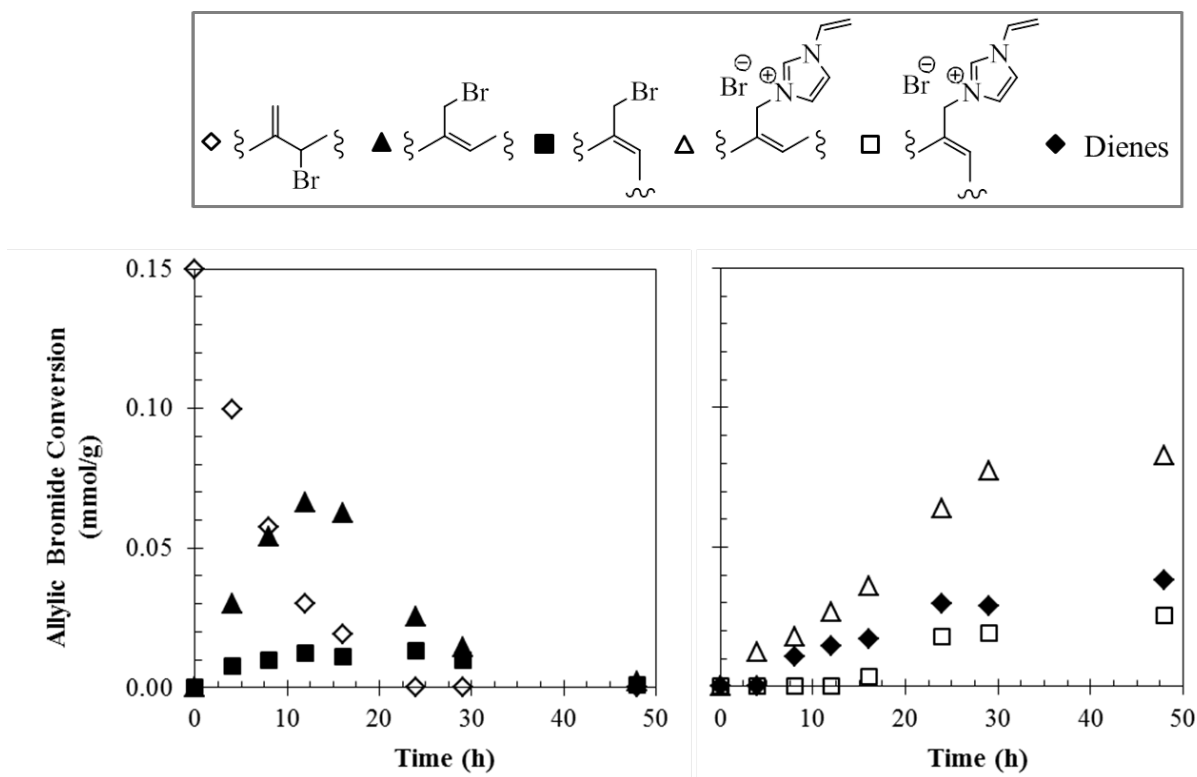


Figure 2.2: N-Alkylation Dynamics of VIm by BIIR in Toluene Solution (100 °C, 6 eq. VIm)

The mechanism for the N-alkylation of N-vinylimidazole by BIIR is similar to that of N-butylimidazole. Isomerization of Exo-Br (**1**) can occur by ionization and ion-pair collapse to yield the *endo*-bromomethyl isomers (**2a**, **2b**), but this process is slow at 100 °C. The dominant isomerization mechanism is S_N2' displacement of allylic bromide by free bromide anion.¹⁶ The preference for *Z*-IIR-VImBr product is due to the preferential conformation of the Exo-Br

functionality and S_N2 displacement of *E/Z-endo*-bromomethyl isomers gives the observed distribution of imidazolium bromide products.

The dynamics of a crosslinking reaction can be monitored using an oscillating biconical disc rheometer operating at fixed temperature, strain and frequency. These rheometers enclose a polymer/curative mixture between two biconical disks and measure the torque required to oscillate the bottom disc, relative to the top disc, as a function of time. The dynamic storage (G') and loss (G'') moduli, as defined in Chapter 1 are determined through calibration of the torque sensing transducer.¹⁷

Figure 2.3 illustrates the cure dynamics of butyl rubber (IIR) and IIR-VImBr in the presence of dicumyl peroxide (DCP). As expected, IIR degraded when heated with DCP, as revealed by a decrease in storage modulus. In contrast, IIR-VImBr showed an increase in storage modulus irrespective of peroxide loading, which is indicative of crosslinking. The best cure performance was observed with 7.5 μmol DCP/g rubber, which appears to have consumed all of the pendant vinylimidazolium unsaturation. A lower peroxide loading produced a lower cure state, while a higher DCP concentration resulted in cure reversion owing to polymer backbone fragmentation. The IIR-VImBr product contains 0.11 mmol/g of N-vinylimidazolium bromide functionality (determined by ¹H NMR) and this functionality was consumed by 7.5 μmol of DCP/g rubber. The peroxide yield of this crosslinking reaction is 14 mmol vinyl content/mmol DCP and this was determined by taking the ratio of N-vinylimidazolium content to the amount of DCP that consumed the vinyl functionality. Peroxide crosslinking of saturated elastomers produces peroxide yields of one, as each peroxide molecule produces one crosslink. The peroxide

crosslinking of IIR-VImBr likely proceeds by oligomerization of the pendant vinyl functionality, as each mole of peroxide consumes greater than one mole of the macromonomer functionality.

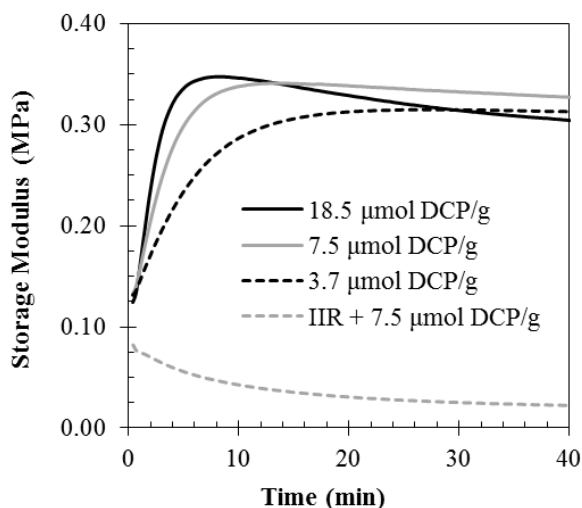


Figure 2.3: Peroxide Crosslinking Dynamics of IIR and IIR-VImBr (160 °C, 1 Hz, 3 °)

As discussed previously, macromonomer derivatives of butyl rubber typically have problems with storage stability and gel formation.^{9, 18, 19} The storage stability of IIR-VImBr and IIR-Acrylate was evaluated by holding samples at 160 °C in the rheometer cavity in the absence of peroxide initiator, yielding the storage modulus data plotted in Figure 2.4. The storage modulus of IIR-VImBr increased by approximately 0.04 MPa over 40 min, while the storage modulus of IIR-Acrylate increases by approximately 0.10 MPa. These tests were extended to 4 h and similar results were observed, showing an increase in the storage modulus of IIR-VImBr by 0.07 MPa, while storage modulus of IIR-Acrylate increased by approximately 0.20 MPa. It appears that gel formation observed for IIR-Acrylate is not a problem for these new macromonomer derivatives. N-vinylimidazolium halide salts have relatively low reactivity towards homopolymerization²⁰,

which proves beneficial, as macromonomers with greater reactivity (such as acrylate functionality) will produce gel over time.

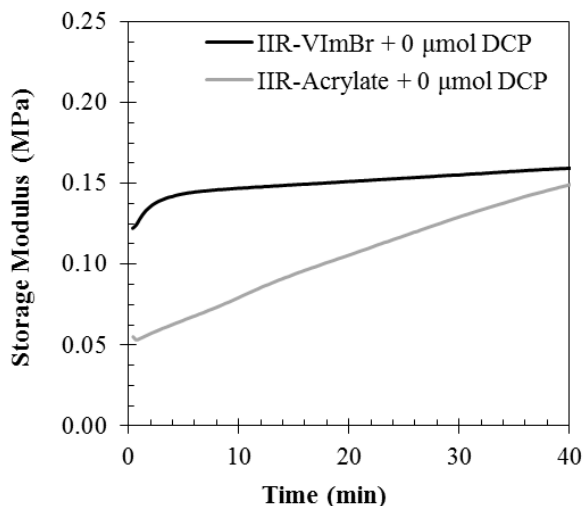


Figure 2.4: Thermal Stability of Macromonomer Derivatives of BIIR (160 °C, 1 Hz, 3 °)

2.3.2 Physical Properties of Crosslinked IIR-VImBr

The susceptibility of ionomers to creep and stress relaxation prevents their use for many engineering applications. In order to study the physical properties of IIR-VImBr, which contains both ionic and covalent networks, comparisons (Scheme 2.2) were made to three other BIIR derivatives: one containing only an ionic network (IIR-BuImBr), another containing only a covalent crosslink network (IIR-Acrylate) and a third containing no ionic or covalent network (IIR-Acetate). To aid in distinguishing crosslinked derivatives from uncrosslinked derivatives, crosslinked derivatives will be referred to as “IIR-VImBr-XL” and “IIR-Acrylate-XL”.

Scheme 2.2: BIIR Derivatives for Crosslink Network Comparison

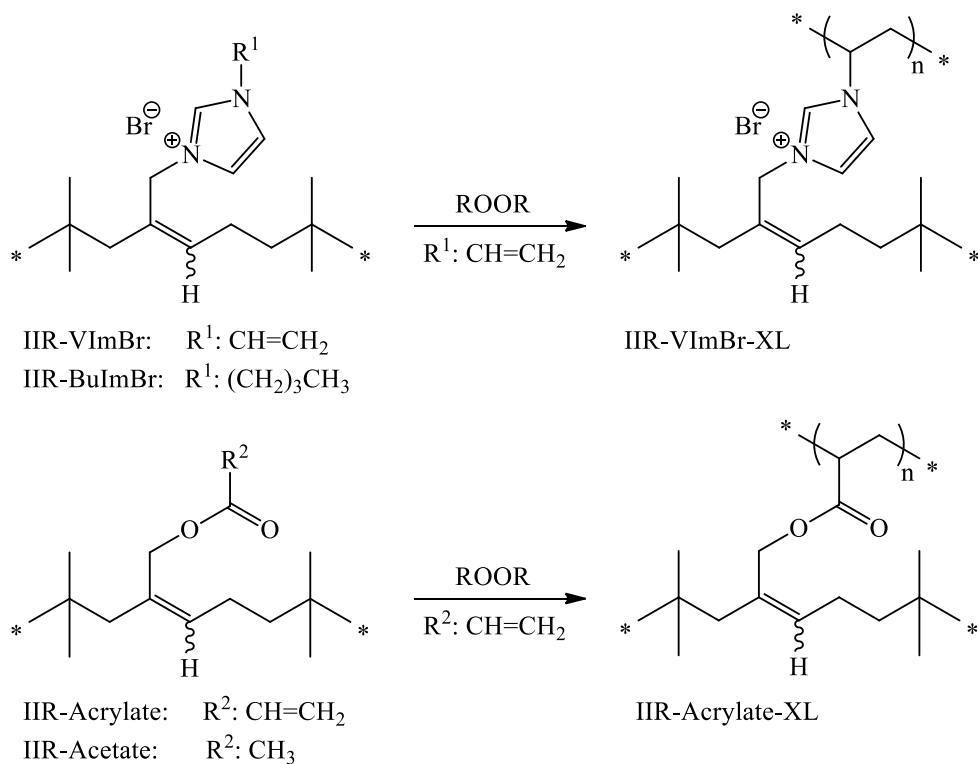


Figure 2.5 displays storage (G') and loss (G'') moduli measurements for samples maintained at 160°C for 25 min. Analysis of this data begins with two unreactive polymers, the non-ionic elastomer IIR-Acetate, and the alkylimidazolium bromide ionomer IIR-BuImBr. These materials are stable in the absence of peroxide, as evidenced by their consistent rheological properties. Although these polymers share the same backbone, both G' and G'' are greater for IIR-BuImBr compared to its non-ionic counterpart. A heightened ability to store inputted energy elastically, as indicated by an elevated G' , is attributed to the ionic crosslink network established by ion-pair aggregation. This ionic crosslink network reduces ionomer chain mobility and reduces relaxation. The elevated G'' of IIR-BuImBr relative to IIR-Acetate indicates that the ionomer has

an increased capacity to dissipate energy viscously. While the ionic network provides a means of energy storage, it is also labile, enhancing energy dissipation in ionomer derivatives.

Peroxide curable IIR derivatives can be prepared by introducing pendant styrenic¹⁸ or acrylate⁹ functionality, whose free radical-initiated oligomerization provides a stable, covalent crosslink network. Figure 2.5 demonstrates the dynamics of IIR-Acrylate crosslinking by 7.5 mmol DCP/g rubber. Initially, the non-ionic macromonomer's storage and loss moduli begin at the same values as those of IIR-Acetate. Upon DCP thermolysis, the storage modulus of IIR-Acrylate rapidly increased to a stable plateau and the loss modulus of IIR-Acrylate rapidly decreased to a stable plateau. The crosslinked product, IIR-Acrylate-XL, was highly elastic, as exemplified by a low loss tangent ($\tan\delta = G''/G'$) value of 0.013.

The IIR-VImBr cure, also illustrated in Figure 2.5, is the first example of a polymer modification that exploits reactive ion-pair functionality. The initial storage and loss moduli values recorded for IIR-VImBr were indistinguishable from those of IIR-BuImBr, indicating that an ionic crosslink network, comprised of N-vinylimidazolium bromide multiplets, was present prior to crosslinking. Initiation of the radical oligomerization of aggregated N-vinylimidazolium bromide functionality increased the ionomer's storage modulus at rates similar to those of IIR-Acrylate, producing IIR-VImBr-XL, with a final G' of 0.36 MPa and a $\tan\delta = 0.12$. Marginal reversion from a G' maximum of 0.38 MPa after 14 min was due to the backbone fragmentation that is commonly observed when all pendant macromonomer functionality is consumed. While a common DCP loading was used for IIR-Acrylate and IIR-VImBr cross-linking for the sake of simplicity, the use of less DCP eliminates this slight cure reversion.

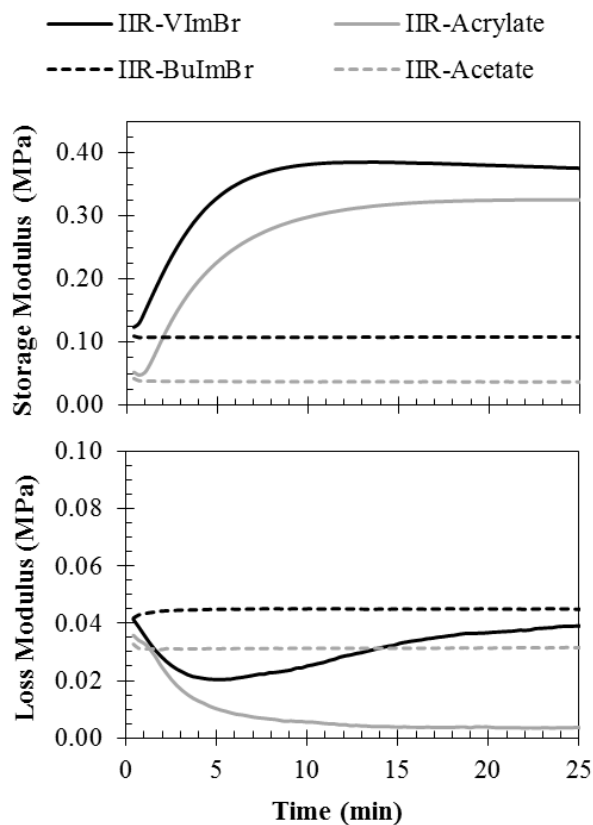


Figure 2.5: Evolution of Storage Modulus and Loss Modulus for IIR-BuImBr, IIR-Acetate, and the Peroxide Cures of IIR-VImBr and IIR-Acrylate (160 °C, 1 Hz, 3°, 7.5 $\mu\text{mol DCP/g}$)

The evolution of G'' over the course of the IIR-VImBr-XL preparation is particularly interesting. The early stages of the ionomer cure proceeded in parallel with IIR-Acrylate, as G'' declined sharply in response to covalent network formation. However, beyond the five minute mark, G'' increased (even as G' continued to rise) continuously toward its initial value of 0.04 MPa, approaching the loss modulus of IIR-BuImBr. This increase in G'' may be caused by molecular weight losses due to cure reversion. Another possibility is that the viscous energy dissipation mechanism provided by ion-pair aggregation operates within IIR-VImBr-XL, as cure reversion is

not observed in G' curve until 14 min. This unique rheological behaviour may impart a number of interesting physical properties to these hybrid ionic/covalent crosslink networks.

The ability of ion-pair association to enhance the reactivity of N-vinylimidazolium bromide groups, and the structure/property relationships of the resulting cross-linked networks, are subjects of ongoing research. Presently, N-vinylimidazolium bromide aggregation has the potential to enhance macromonomer oligomerization, in IIR-VImBr by concentrating vinyl groups within the ionomer multipliers. During the crosslinking process, the labile ionic network originally within IIR-VImBr is converted into a stable covalent network with aggregated N-alkylimidazolium bromide functionality. The physical properties of this hybrid ionic/covalent network are of interest as covalent cross-links likely derive little strength from ionic associations of constituent N-alkylimidazolium bromide groups. That is, the strength of a covalent cross-link is unlikely to benefit from interactions between its own ion-pairs.

The temperature sweep data provided in Figure 2.6 reveal more of the character of hybrid ionic/covalent polymer networks. Similar to other elastomeric ionomers²¹, the storage modulus of IIR-BuImBr declined with increasing temperature, owing to reduced strength of the ionic network. When compared to IIR-Acetate, the G' of IIR-BuImBr was 0.14 MPa greater at 100°C, but just 0.04 MPa higher at 200°C. The non-ionic thermoset, IIR-Acrylate-XL, behaved opposite to that of IIR-BuImBr, as its storage modulus increased significantly over the recorded temperature range (Figure 2.6). This is consistent with standard models of covalent thermoset behaviour, whose entropically-driven elasticity responds with greater restorative force as temperature is increased.²² The response of IIR-VImBr-XL to increased temperature is

remarkable in terms of its insensitivity. The storage modulus, being an order of magnitude greater than the loss modulus, dominates the material's response to an applied strain, and its near constant value of 0.36 MPa clearly differentiates it from IIR-Acrylate-XL and IIR-BuImBr. It is assumed that losses in ionic network strength are offset by increases in covalent network strength, as temperature is increased. As such, the hybrid ionic/covalent network provides material performance with beneficial aspects of conventional ionomers and covalent thermosets.

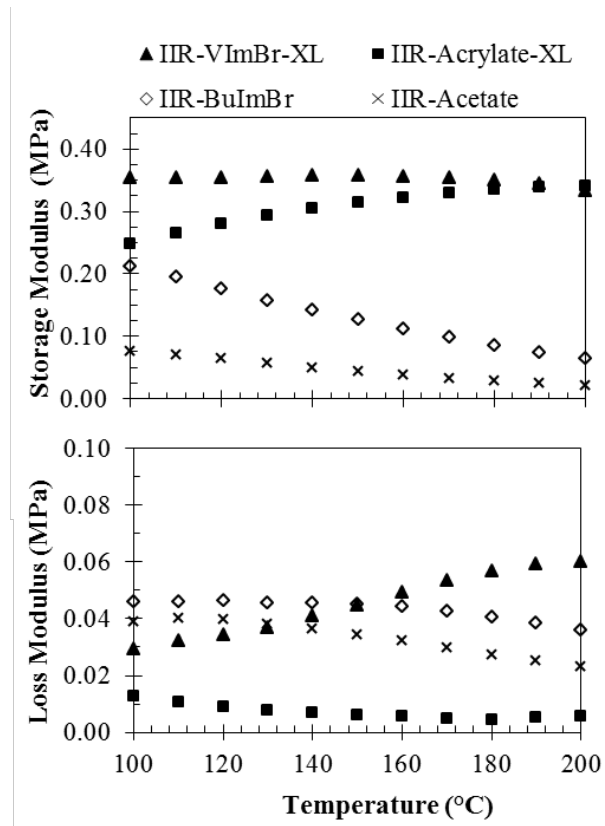


Figure 2.6: Temperature Sweep of G' and G'' for IIR-BuImBr, IIR-Acetate, IIR-VImBr-XL and IIR-Acrylate-XL (1 Hz, 3°)

Monitoring the response of an elastomer to dynamic, oscillatory deformations, such as the temperature sweeps illustrated in Figure 2.6, provides valuable insight into the network structure. However, monitoring the response of a sample that is subjected to a constant strain deformation gives insight into relaxation properties. Figure 2.7 provides modulus measurements as a function of time for samples held at 100 °C and a fixed strain of 2° arc. As expected, the non-crosslinked polymers, IIR-Acetate and IIR-BuImBr, demonstrated a high degree of stress relaxation. Without a covalent crosslink network to prevent polymer chains from flowing through their entanglements, the modulus of IIR-Acetate declined continuously, reaching zero stress in less than one minute. Relaxation of IIR-BuImBr was considerably slower, but the labile nature of the ionic network is clearly evident. In contrast, the stable covalent network within IIR-Acrylate-XL prevented flow of polymer chain segments, resulting in a near constant modulus. In keeping with its hybrid structure, the response of IIR-VImBr-XL to a constant strain was intermediate between that of IIR-BuImBr and IIR-Acrylate-XL. The modulus of IIR-VImBr-XL declined throughout the measurement, but did not approach zero, rather, the modulus seems to approach that of IIR-Acrylate-XL. This suggests that the network of ion-pair aggregates is subject to relaxation, while the covalent network maintains a stable response to applied strains.

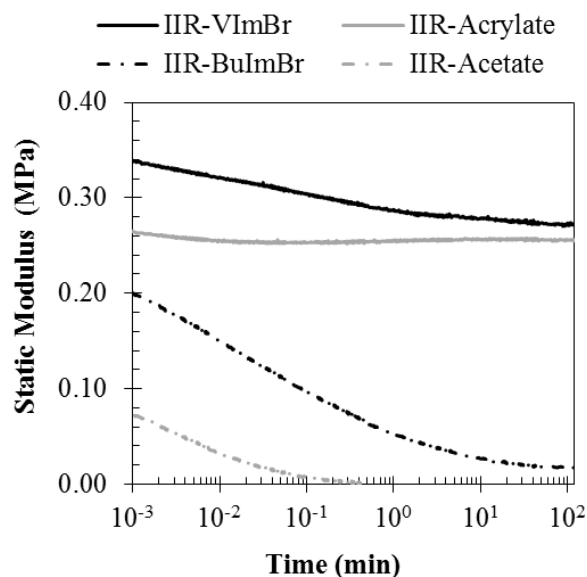


Figure 2.7: Stress Relaxation of IIR-BuImBr, IIR-Acetate, IIR-VImBr-XL and IIR-Acrylate-XL (100 °C, 2 °)

Further characterization of this crosslink network was done by measuring a number of other physical properties and they are quantified in Table 2.1. Comparison of IIR-VImBr-XL to IIR-BuImBr and IIR-Acrylate-XL will help distinguish if physical properties are derived from the ionic crosslink network or the covalent crosslink network. IIR-Acetate was not considered for further comparison as it is not crosslinked and poor physical properties were expected. Peroxide crosslinking has been used to establish a covalent crosslink network in addition to the ionic crosslink network in IIR-VImBr-XL. The change in storage modulus for IIR-VImBr, due to peroxide curing, is similar to that of IIR-Acrylate, which suggests that the covalent crosslink networks in these materials have similar crosslink density. Tensile properties of IIR-VImBr-XL show low elongations and low tensile stress at break, similar to IIR-Acrylate-XL. This is likely a

consequence of the tight, covalent crosslink network that does not allow for flow of individual polymer chains through entanglements. The Young's modulus of IIR-VImBr-XL is quite high at 0.78 MPa and is closer in range to that of IIR-BuImBr. Young's modulus is calculated over a low elongation (0 – 0.2 mm) and ionic crosslinks are likely capable of reinforcing the material at these low strains, but become weaker as the strain is increased. The glass transition temperature of these derivatives was measured by differential scanning calorimetry (DSC). The glass transition temperatures remain constant, and on the same order as polyisobutylene ($T_g = -60\text{ }^\circ\text{C}$), regardless of the functionality incorporated into the polymer. No thermal transitions were observed for ionic aggregates at higher temperatures, which has been reported for other DSC studies on ionic multiplet glass transition temperatures.¹

Table 2.1: Physical Properties IIR-BuImBr, IIR-VImBr-XL and IIR-Acrylate-XL

Physical Property	IIR-BuImBr	IIR-VImBr-XL	IIR-Acrylate-XL
$\Delta G'$ (MPa)	0 ± 0.01	0.23 ± 0.02	0.26 ± 0.02
Young's Modulus (MPa)	0.72 ± 0.11	0.78 ± 0.03	0.45 ± 0.07
Maximum Tensile Stress (MPa)	9.3 ± 0.5	1.9 ± 0.2	0.7 ± 0.1
Elongation at Break (%)	2470 ± 130	230 ± 10	250 ± 20
Glass Transition ($^\circ\text{C}$, DSC)	-63 ± 2	-63 ± 2	-64 ± 2
Compression Set (%)	56 ± 6	6.2 ± 0.6	2.3 ± 0.2

Compression set is another measure of relaxation that is often used in the rubber industry. A compressive strain is applied axially to a cylindrical rubber sample for a prolonged period, after

which the percent of the strain that is recovered is measured. A high extent of recovery, where dimensions of the cylinder are similar to the starting dimensions, gives a low compression set value, and is generally desired as it reflects the resistance of the material to permanent deformation. Typically the stable covalent bonds formed during peroxide crosslinking result in low compression set values as observed for IIR-VImBr-XL and IIR-Acrylate-XL (Table 2.1). The high compression set value recorded for IIR-BuImBr is consistent with the extent of stress relaxation (Figure 2.7) observed when subjecting the ionomer to a steady shear strain.

2.4 Conclusion

A reactive ionomer derivative of BIIR has been prepared by the N-alkylation of N-vinylimidazole. The toluene-solution reaction yields IIR-VImBr with an ion-content of 0.11 mmol/g after 50 h of reaction. Characterization of the model compound PMN-VImBr by ^1H NMR spectroscopy shows excellent agreement with the ^1H NMR spectrum of IIR-VImBr. Peroxide crosslinking of IIR-VImBr occurs quickly to yield a thermoset material, IIR-VImBr-XL, which contains an ionic crosslink network as well as a covalent crosslink network. There is little tendency for this macromonomeric ionomer to form gel upon standing at room temperature for prolonged periods, and crosslinking in the absence of peroxide at 160 °C is lessened when compared to macromonomers such as IIR-Acrylate. Changes in storage modulus for IIR-VImBr and IIR-Acrylate are quite similar, even though IIR-VImBr does not tend to polymerize well, and ion-pair aggregation may promote this crosslinking reaction.

These hybrid networks containing ionic and covalent crosslink networks have unique physical properties. Stress relaxation is not as extensive for IIR-VImBr-XL as for IIR-BuImBr, which

contains only ionic crosslinks. Tensile properties IIR-VImBr-XL are intermediate between IIR-BuImBr and IIR-Acrylate-XL. Compression set measurements for peroxide crosslinked articles is generally quite low and IIR-VImBr-XL follows this trend, again indicating that the covalent crosslink network provides strength to the material in cases where the ionic crosslink network is labile.

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Chapter 3: Composition Distribution Study

3.1 Introduction

The previous chapter described the synthesis of IIR-VImBr, and provided a comparison of this reactive ionomer's properties relative to other isobutylene-based materials. This chapter is concerned with the synthesis and physical properties of materials with different overall compositions and composition distributions. These studies began with ionomers prepared by N-alkylation of N-vinylimidazole and N-butylimidazole mixtures, whose total ion-pair contents were held constant while the proportion of vinyl and alkyl substituents was varied systematically. Xiao et al. showed that peroxide cured extents observed for acrylate ester derivatives of BIIR varied linearly with acrylate content, with the remaining allylic bromide content being converted to stearate esters.¹ Therefore, the physical properties of a macromonomer derivative can be tailored for a given application by controlling the acrylate and stearate ester yield of a BIIR esterification. Extension of this approach to reactive ionomers may provide similar insights to the IIR-VImBr derivatives.

Mixed alkylation products contain a uniform composition distribution in which each polymer chain has the same average amount of pendant N-vinylimidazolium bromide and N-butylimidazolium bromide functionalities. An alternate composition distribution can be prepared by mixing two pure materials, IIR-VImBr and IIR-BuImBr in different proportions. In this case, total ion-pair concentrations were held constant, and average vinyl and alkyl substituent concentrations were controlled. However, only IIR-VImBr chains are capable of peroxide cure. IIR-BuImBr is not crosslinked under the action of peroxide initiators, but rather undergoes mild

degradation. Therefore, peroxide cured blends of these two ionomers yield unusual interpenetrating networks (IPNs), in which the hybrid covalent-ionic network of IIR-VImBr-XL is interwoven with the ionic network of IIR-BuImBr. Insight into how these networks interact was gained by independent studies of material properties, and through comparison to the mixed alkylation products described above.

Two other composition distributions are also described in this chapter. Interpenetrating networks comprised of IIR-VImBr-XL and IIR were prepared to determine the properties of a hybrid ionic/covalent network in combination with a non-ionic, non-crosslinked component. The last materials to be tested were IPNs prepared from a non-ionic, covalent network in combination with IIR-BuImBr. In this case, IPNs were synthesized from a dodecyl itaconate ester derivative of bromobutyl rubber, IIR-DDI, which is a macromonomer that cures to a covalent network lacking an ionic aggregation component.

3.2 Experimental

Materials. N-vinylimidazole (VIm, 99+%), N-butylimidazole (BuIm, 98%), 1-dodecanol (98%), itaconic anhydride (95%), tetra-N-butylammonium hydroxide (TBAOH, 1.0 M in methanol), tetra-N-butylammonium bromide (TBAB, 99%), tetra-N-butylammonium acetate (TBAAc, 97%), chloroform-*d* (99.8%D), methanol-*d*₄ (99.8%D), toluene-*d*₆ (99.6%D) and dicumyl peroxide (DCP, 98%) were used, as received, from Sigma Aldrich (Oakville, Ontario). BIIR (BB 2030, $M_n = 400\ 000$ g/mol, polydispersity = 1.5, 0.15 mmol allylic bromide functionality/g BIIR) and

IIR (RB 301, $M_n = 400\,000$ g/mol, polydispersity = 1.5, 0.50 mmol isoprene functionality/g IIR) were used as supplied by LANXESS Inc. (Sarnia, Ontario).

Synthesis of IIR-VImBr. BIIR (120 g, 18.0 mmol allylic bromide) was dissolved in toluene (1200 mL, 10 wt%) and heated to 100 ± 2 °C. VIm (10.16 g, 108.0 mmol, 6 eq.) was then added to the solution and allowed to react for 50 h. The N-alkylation product was obtained by precipitation in excess acetone and purified by dissolution/precipitation using tetrahydrofuran/acetone and dried *in vacuo*. IIR-VImBr was produced in 75% yield corresponding to an ion content of 0.11 mmol/g. The degree of N-alkylation was quantified by the integration of normalized proton ^1H NMR spectra to an estimated accuracy of ± 5 %. ^1H NMR ($\text{CDCl}_3 + 5$ wt% CD_3OD) for IIR-VImBr: δ 11.53 (s, 1H, $-\text{N}^+-\text{CH}-\text{N}-$), δ 7.61 (s, 1H, $-\text{N}^+-\text{CH}=\text{CH}-\text{N}-$), δ 7.42 (dd, 1H, $-\text{N}-\text{CH}=\text{CH}_2$), δ 5.80 (dd, 1H, $\text{N}-\text{CH}=\text{CH}-\text{H}_{\text{trans}}$), δ 5.41 (dd, 1H, $\text{N}-\text{CH}=\text{CH}-\text{H}_{\text{cis}}$), found for the *Z*-isomer: δ 7.16 (s, 1H, *Z*, $-\text{N}^+-\text{CH}=\text{CH}-\text{N}-$), δ 5.69 (t, 1H, *Z*, $\text{CH}_2-\text{C}=\text{CH}-\text{CH}_2$), δ 4.91 (s, 2H, $-\text{C}-\text{CH}_2-\text{N}^+$), found for the *E*-isomer: δ 7.20 (s, 1H, *E*, $-\text{N}^+-\text{CH}=\text{CH}-\text{N}-$), δ 5.68 (t, 1H, *E*, $\text{CH}_2-\text{C}=\text{CH}-\text{CH}_2$), δ 4.84 (s, 2H, *E*, $-\text{C}-\text{CH}_2-\text{N}^+$). ^1H NMR for conjugated dienes: δ 5.98 (d, 1H, *exo*-diene), δ 5.92 (d, 1H, *endo*-diene). ^1H NMR for residual isoprene: δ 5.04 (t, 1H, $\text{CH}_3-\text{C}=\text{CH}-\text{CH}_2-$).

Synthesis of IIR-BuImBr. BIIR (120 g, 18.0 mmol allylic bromide) was dissolved in toluene (1200 mL, 10 wt%) and heated to 100 ± 2 °C. BuIm (13.41 g, 108.0 mmol, 6 eq.) was then added to the solution and allowed to react for 16 h. The N-alkylation product was obtained by precipitation in excess acetone and purified by dissolution/precipitation using tetrahydrofuran/acetone and dried *in vacuo*. IIR-BuImBr was produced in 95% yield

corresponding to an ion content of 0.14 mmol/g. The degree of N-alkylation was quantified by the integration of normalized proton ^1H NMR spectra to an estimated accuracy of $\pm 5\%$. This procedure followed the work by Parent *et al.*² ^1H NMR ($\text{CDCl}_3 + 5\text{ wt}\% \text{CD}_3\text{OD}$) for IIR-BuImBr: δ 4.89 (s, 2H, $=\text{C}-\text{CH}_2-\text{N}^+$, *Z*-isomer), δ 4.82 (s, 2H, $=\text{C}-\text{CH}_2-\text{N}^+$, *E*-isomer), δ 4.35 (t, 2H, $\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$). This ^1H NMR spectrum was consistent with previous work by Parent *et al.*²

Synthesis of 4-(dodecyloxy)-2-methylene-4-oxobutanoic acid. Itaconic anhydride (3.0 g, 26.8 mmol) and 1-dodecanol (4.54 g, 24.4 mmol) were dissolved in toluene and heated to $85 \pm 2\text{ }^\circ\text{C}$ and allowed to react for 4 hours. Toluene and excess itaconic anhydride were removed by Kugelrohr distillation (80 Pa, $60\text{ }^\circ\text{C}$). This procedure followed that of previous work by Whitney *et al.*³ ^1H NMR (CDCl_3) for 4-(dodecyloxy)-2-methylene-4-oxobutanoic acid: δ 6.44 (s, 1H, $\text{HO}-\text{C}(=\text{O})-\text{C}(=\text{CH}-\text{H})-\text{CH}_2$), δ 5.83 (s, 1H, $\text{HO}-\text{C}(=\text{O})-\text{C}(=\text{CH}-\text{H})-\text{CH}_2$), δ 4.10 (t, 2H, $-\text{O}-\text{CH}_2-\text{CH}_2-$), δ 3.34 (s, 2H, $-\text{C}(=\text{CH}_2)-\text{CH}_2-\text{C}(=\text{O})-\text{O}$), δ 1.62 (qi, 2H, $\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-$), δ 1.25 (m, 18H, aliphatic CH_2 groups), δ 0.88 (t, 3H, $-\text{CH}_2-\text{CH}_2-\text{CH}_3$). This ^1H NMR spectrum was consistent with previous work by Whitney *et al.*³

Synthesis of Tetra-N-butylammonium 4-(dodecyloxy)-2-methylene-4-oxobutanoate (TBADDI). 4-(Dodecyloxy)-2-methylene-4-oxobutanoic acid (6.56 g, 22.0 mmol) was mixed with TBAOH (22 mL, 1.0 M in MeOH, 22.0 mmol) and stirred for 30 min at room temperature. Methanol was removed by Kugelrohr distillation at room temperature and 80 Pa to yield solid white crystals. This procedure followed that of previous work by Whitney *et al.*³

Synthesis of IIR-DDI. BIIR (120 g, 18.0 mmol allylic bromide) was dissolved in toluene (200 mL, 10 wt%) and heated to 85 ± 2 °C and TBAB (2.90 g, 9.0 mmol, 0.5 eq.) was then added to the solution to isomerize from **1** to **2a/2b**, for 2 h. TBAAc (1.63 g, 5.4 mmol, 0.3 eq.) was then added to the solution and allowed to react for 1 h. TBADDI (7.77 g, 14.4 mmol, 0.8 eq.) was added to the solution and allowed to react for 2 hours to ensure complete allylic bromide conversion. The esterification product was obtained by precipitation in excess acetone and purified by dissolution/precipitation using tetrahydrofuran/acetone and dried *in vacuo*. The product contained 0.11 mmol/g of dodecyl itaconate functionality, with the remaining 0.04 mmol/g comprising acetate functionality. This procedure was adapted from previous work by Whitney *et al.*³ ¹H NMR (CDCl₃) for IIR-DDI: δ 4.70 (t, 2H, =CH₂-O-C(=O)-, *Z*-ester), δ 4.60 (t, 2H, =CH₂-O-C(=O)-, *E*-ester). ¹H NMR for IIR-Acetate: δ 4.58 (t, 2H, =CH₂-O-C(=O)-CH₃, *Z*-ester), δ 4.51 (t, 2H, =CH₂-O-C(=O)-CH₃, *E*-ester). ¹H NMR for conjugated dienes: δ 6.01 (d, 1H, *exo*-diene), 5.95 (d, 1H, *endo*-diene). ¹H NMR for residual isoprene: δ 5.07 (t, 1H, CH₃-C=CH-CH₂). This ¹H NMR spectrum was consistent with that of previous work by Whitney *et al.*³

Synthesis of Mixed Alkylation Products Containing 25% N-vinylimidazolium Bromide and 75% N-butylimidazolium Bromide Functionality. BIIR (45.0 g, 6.75 mmol) was dissolved in toluene (450 mL, 10 wt%) and heated to 100 ± 2 °C. VIm (2.10 g, 24.98 mmol, 3.70 eq.) and BuIm (2.26 g, 18.22 mmol, 2.70 eq.) were then added to the solution and allowed to react for 24 h. The N-alkylation product was obtained by precipitation in excess acetone and purified by dissolution/precipitation using tetrahydrofuran/acetone and dried *in vacuo*. The product contained 0.04 mmol/g N-vinylimidazolium bromide grafts and 0.11 mmol/g N-butylimidazolium

bromide grafts. The degree of N-alkylation was quantified by the integration of normalized proton ^1H NMR spectra to an estimated accuracy of $\pm 5\%$. ^1H NMR spectra for these compositions can be found in Figure A.1, in Appendix A.

Synthesis of Mixed Alkylation Products Containing 50% N-vinylimidazolium Bromide and 50% N-butylimidazolium Bromide Functionality. BIIR (45.0 g, 6.75 mmol) was dissolved in toluene (450 mL, 10 wt%) and heated to 100 ± 2 °C. VIm (3.02 g, 32.06 mmol, 4.75 eq.) and BuIm (2.26 g, 8.44 mmol, 1.25 eq.) were then added to the solution and allowed to react for 24 h. The N-alkylation product was obtained by precipitation in excess acetone and purified by dissolution/precipitation using tetrahydrofuran/acetone and dried *in vacuo*. The product contained 0.06 mmol/g N-vinylimidazolium bromide grafts and 0.08 N-butylimidazolium bromide grafts. The degree of N-alkylation was quantified by the integration of normalized proton ^1H NMR spectra to an estimated accuracy of $\pm 5\%$. ^1H NMR spectra for these compositions can be found in Figure A.1, in Appendix A.

Synthesis of Mixed Alkylation Products Containing 75% N-vinylimidazolium Bromide and 25% N-butylimidazolium Bromide Functionality. BIIR (45.0 g, 6.75 mmol) was dissolved in toluene (450 mL, 10 wt%) and heated to 100 ± 2 °C. VIm (3.56 g, 37.80 mmol, 5.60 eq.) and BuIm (0.34 g, 2.70 mmol, 0.40 eq.) were then added to the solution and allowed to react for 24 h. The N-alkylation product was obtained by precipitation in excess acetone and purified by dissolution/precipitation using tetrahydrofuran/acetone and dried *in vacuo*. The product contained 0.11 mmol/g N-vinylimidazolium bromide grafts and 0.04 mmol/g N-butylimidazolium bromide grafts. The degree of N-alkylation was quantified by the integration of normalized

proton ^1H NMR spectra to an estimated accuracy of $\pm 5\%$. ^1H NMR spectra for these compositions can be found in Figure A.1, in Appendix A.

Preparation of Interpenetrating Networks. One rubber containing vinyl groups (IIR-VImBr or IIR-DDI, 120 g) was dissolved in toluene (1200 mL, 10 wt%). The non-vinyl containing component of the mixture (IIR-BuImBr or IIR, 120 g) was dissolved in toluene (1200 mL, 10 wt%). In the case of IIR, it was previously dissolved in toluene and precipitated in acetone to remove additives. The vinyl containing rubber and the non-vinyl containing rubber were mixed in toluene solution according to the masses shown in Table 3.1. The solutions were mixed for 12 h, and precipitated in excess acetone. They were purified by dissolution/precipitation tetrahydrofuran/acetone and dried *in vacuo*. ^1H NMR spectra for these compositions can be found in Figures A.1 - A.4 in Appendix A.

Table 3.1: Toluene Solution Mass for Preparing IPN Formulations

Composition	Mass of Vinyl Solution (g)	Mass of Non-vinyl Solution (g)
25% Vinyl Content	145	325
50 % Vinyl Content	275	200
75% Vinyl Content	350	90

Preparation of Cured Macrosheets. A 40.0 g batch of dried elastomer was coated with the required amount of a solution of DCP in acetone and allowed to dry before being passed through

a two roll mill ten times. A 5.0 g sample of the mixed compound was cured in the rheometer cavity at 160 °C, at a 3° oscillation arc and a frequency of 1 Hz to monitor cure dynamics. The remaining 33.0 g of the mixture was sheeted with a two-roll mill and compression molded at 160 °C and 20 MPa for 25 min ($5t_{1/2}$ for DCP³⁶).⁴ The sheeted products had a thickness of 2.00 ± 0.05 mm.

Preparation of Cured Cylinders for Compression Set. The remaining 2.0 g of the 40.0 g batch were placed inside a cylindrical mold with a diameter of 14.0 mm and a height of 12.5 mm. The samples were cured at 160 °C for 25 min. The final cylinders had a diameter of 14 ± 0.1 mm and a height of 12.5 ± 0.2 mm.

Analysis. NMR characterization was done on a Bruker AM600 instrument and a Bruker AM500 instrument with chemical shifts (δ) reported relative to tetramethylsilane in ppm.

Rheological characterization was carried out in an oscillatory rheometer (Advanced Polymer Analyzer 2000, Alpha Technologies) operating in a parallel plate configuration. A 5.0 g sample of the uncured material was coated with the required amount of a solution of DCP in acetone and allowed to dry before being passed through a two roll mill ten times. The mixed compound was cured in the rheometer cavity at 160 °C for 60 min, at a 3° oscillation arc and a frequency of 1 Hz. Stress relaxation measurements were conducted at 100 °C with a strain of 2° for 5 min. Temperature sweeps were conducted from 100 °C to 200 °C at a frequency of 1 Hz and a 3° oscillation arc.

Tensile strength data were acquired using an INSTRON Series 3360 universal testing instrument, operating at a crosshead speed of 500 mm/min at 23 ± 1 °C.⁵ Young's modulus was found by calculating the slope of the stress (MPa) vs. strain (mm/mm) curve from 0 mm to 0.2 mm of extension. Dogbones were cut from the specimen cutter described in ASTM D4482.⁶ Five replicate measurements were made for each sample to test the precision of the compounding and physical testing procedures.

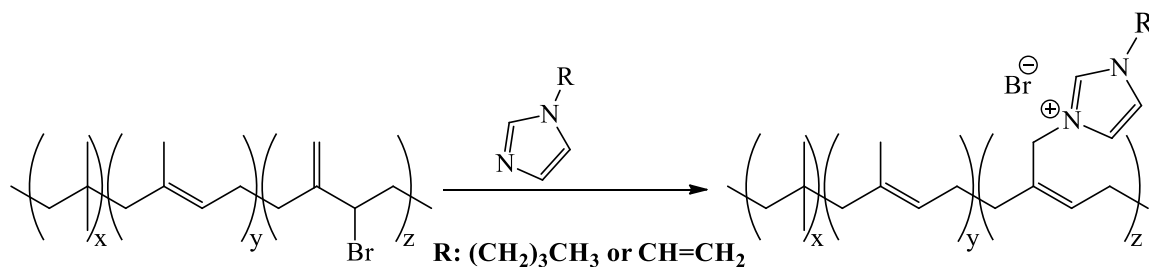
Compression set measurements were carried out using a pneumatic press. Sample height was measured and samples, as well as stainless steel spacers, were placed on a stainless steel plate inside the press. The spacer height was 6.44 mm, corresponding to an applied strain of 45 %. The apparatus was compressed with 3.5 MPa and left for 22 h. After 22 h, the samples were removed and rest for 0.5 h before the final height of the cylinders was measured.⁷

3.3 Results and Discussion

3.3.1 Mixed N-Alkylation Products of VIm and BuIm

This section describes the synthesis, vulcanization and physical properties of isobutylene-based imidazolium bromide ionomers bearing different proportions of vinyl and alkyl substituents (Scheme 3.1). These mixed alkylation products have a constant ion-pair concentration, but different peroxide-curing reactivity. The imidazolium bromide groups bearing butyl substituents are largely unreactive to peroxide modification, but ion-pairs bearing vinyl substituents undergo relatively efficient radical oligomerization, thereby producing a thermoset, covalent crosslink network, in addition to the ionic crosslink network established by ion-pair aggregation.

Scheme 3.1: Mixed N-Alkylation of N-vinylimidazole and N-butylimidazole by BIIR



All mixed alkylation reactions were carried out in toluene solution reaction at 100 °C and the nucleophile concentrations were optimized to introduce the desired amount of N-butylimidazolium bromide functionality and N-vinylimidazolium bromide functionality. Allylic bromide conversions were quantitative in each case, yielding ion contents of about 0.12 mmol/g, and conjugated diene contents of approximately 0.03 mmol/g. Samples were classified according to the proportion of vinyl groups amongst the 0.12 mmole/g of ionic functionality. For example, IIR-BuImBr contained no vinyl content and is referred to as “0% vinyl” whereas each ion-pair in IIR-VImBr contains a vinyl group, and this material is referred to as “100% vinyl”.

Free radical oligomerization of pendant N-vinylimidazolium bromide functionality was used to establish a covalent crosslink network, as described in Chapter 2. The initiator concentration used to cure each sample was scaled according to the N-vinylimidazolium bromide content. Throughout this work, a peroxide dosage of 0.07 mmole DCP per mmole N-vinylimidazolium bromide was employed, thereby maintaining a constant ratio of free radical generating species to peroxide-curable species. Additionally, materials labeled “0% vinyl” did not receive a peroxide

dose, since they have no peroxide-curable functionality and degrade under the action of free radical initiators.

Peroxide curing dynamics and yields for these mixed alkylation products are illustrated in Figure 3.1, along with the physical properties of the resulting thermosets. Consistent with previous studies of acrylate and styrenic macromonomers, the extent of peroxide cure was sensitive to the amount of vinyl functionality in the imidazolium ionomer. The change in storage modulus ($\Delta G' = G'_{\max} - G'_{\min}$; Figure 3.1a) was nearly a linear function of VImBr content, and decreases in $\tan \delta$ (Figure 3.1b) were consistent with improved material elasticity.

Figure 3.1c illustrates the storage modulus of cured mixed alkylation products as a function of temperature. Note that these materials were cross-linked in the rheometer cavity for 60 min at 160 °C, as described above. While the hybrid network within IIR-VImBr-XL provided a fairly stable storage modulus, with a slight decrease at high temperature, over the 100-200 °C range, the non-covalent network within IIR-BuImBr weakened significantly, as discussed in Chapter 2. The mixed alkylation products provided storage modulus values intermediate between the pure component materials. Therefore, the dynamic properties of these materials can be tailored by varying the relative amounts of vinyl and alkyl functionality in the ionomer.

Similar conclusions can be drawn from the stress relaxation data and compression set measurements. Figure 3.1d shows the static modulus of cured materials as a function of time, measured as the polymers are subjected to a small, constant shear strain. A decline in static modulus is a result of stress relaxation, brought on by movement of chain segments in response to

the applied strain. Unstable polymer networks can relax completely to give a static modulus (measured stress / applied strain) of zero, while tight covalent networks can provide a stable static modulus, since the relaxation of chain segments is restricted. Compression set measurements yielding the data presented in Figure 3.1e are complementary to stress relaxation data, in that they measure the irreversible deformation incurred by a sample that is subjected to a constant compressive strain. Both data sets show that mixed alkylation products provide intermediate relaxation behavior compared to IIR-VImBr-XL and IIR-BuImBr, except for the “75% vinyl” sample. It appears that this composition provides similar resistance to relaxation as IIR-VImBr-XL with less vinyl content.

Static tensile data, for representative curves, are presented in Figure 3.1f in the form of engineering stress-strain plots. These data also demonstrate the potential to tailor material properties by varying vinyl contents. Higher covalent network contributions result in lower elongations at break and as a consequence, the tensile stress at break also decreases. The insensitivity of the Young’s modulus of crosslinked mixed alkylation products to vinyl content is particularly interesting. Young’s modulus is calculated from the slope of a stress-strain plot at zero elongation. Values calculated from the data shown in Figure 3.1f fell between 0.72 MPa for IIR-BuImBr and 0.78 MPa for IIR-VImBr. Therefore, the initial stiffness of these ionomer systems is not a function of covalent network strength. Rather, it is the ionic network strength that dictates tensile properties at low elongation.