

Effects of Leaving Group Ability and Microstructure on the Reactivity of Halogenated
Poly(isobutylene-*co*-isoprene)

By

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Abstract

Halogenation of poly(isobutylene-*co*-isoprene) (IIR) increases its reactivity towards sulphur and other nucleophiles. Currently brominated (BIIR) and chlorinated (CIIR) derivatives are commercially available; however, an iodinated derivative has been briefly investigated. The effects of leaving group ability and microstructure on the reactivity of halogenated poly(isobutylene-*co*-isoprene) were studied to put iodobutyl rubber reactivity into context and to compare existing commercial products to their isomeric derivatives.

Polymers containing halomethyl (*r*-CIIR, *r*-BIIR, *r*-IIIR) isomers of butyl rubber were prepared from as-received BIIR to compare the effect of leaving group on thermal stability and reactivity towards nucleophilic substitution. The polymer containing (*E,Z*)-*endo*-iodomethyl isomers (*r*-IIIR) readily underwent nucleophilic substitution at low temperatures; however, it was sensitive towards dehydrohalogenation at temperatures above 65°C. At temperatures between 100°C and 135°C, the bromomethyl derivative (*r*-BIIR) demonstrated the best balance between reactivity toward nucleophilic substitution and dehydrohalogenation. Exceptional thermal stability at temperatures up to 190°C was displayed by the chloromethyl derivative (*r*-CIIR); however, it was unreactive at low temperatures towards certain nucleophiles. This lack of reactivity shown by *r*-CIIR was not consistent with all nucleophiles, as reaction dynamics with TBAAc display its variable reactivity towards nucleophilic substitution with results parallel to those of *r*-BIIR.

Exo-methylene allylic halides (Exo-Br, Exo-Cl) and (*E,Z*)-*endo*-halomethyl (r-BIIR, r-CIIR) isomers were vulcanized with sulphur to determine the effect of microstructure on reactivity. Results showed a clear effect of microstructure on the ability to cure with sulphur. While the Exo-Cl isomer has no ability to cure, when rearranged to its (*E,Z*)-*endo*-chloromethyl isomer curing occurs readily. Both the Exo-Cl and (*E,Z*)-*endo*-bromomethyl isomers readily vulcanize in the presence of sulphur, however Exo-Br cures to a greater extent.

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Abbreviations

IIR	- Poly(isobutylene-co-isoprene)
BIIR	- Brominated poly(isobutylene-co-isoprene)
r-BIIR	-Rearranged Brominated poly(isobutylene-co-isoprene) consisting of (<i>E,Z</i>)- <i>endo</i> -bromomethyl isomers
BPMN	- Brominated 2,2,4,8,8-pentamethyl-4-nonene
CIIR	- Chlorinated poly(isobutylene-co-isoprene)
r-CIIR	-Rearranged Chlorinated poly(isobutylene-co-isoprene) consisting of (<i>E,Z</i>)- <i>endo</i> -chloromethyl isomers
Exo-Cl	- <i>exo</i> -methylenechloride isomer of CIIR
CPMN	- Chlorinated 2,2,4,8,8-pentamethyl-4-nonene
r-IIIR	-Iodinated poly(isobutylene-co-isoprene) consisting of mainly (<i>E,Z</i>)- <i>endo</i> -iodomethyl isomers
IPMN	- Iodinated 2,2,4,8,8-pentamethyl-4-nonene
NMR	- Nuclear magnetic resonance
MS	- Mass Spectrometry
TBAB	- Tetra- <i>n</i> -butylammonium bromide
TBAC	- Tetra- <i>n</i> -butylammonium chloride
TBAI	- Tetra- <i>n</i> -butylammonium iodide
TBAAc	- Tetra- <i>n</i> -butylammonium acetate
BuIm	- N-Butylimidazole
s	- Singlet

d - Doublet
t - Triplet
phr - Parts per hundred rubber

Chapter 1. Introduction

1.1 Poly(isobutylene-co-isoprene) Rubber

Poly(isobutylene-co-isoprene) rubber, or butyl rubber (IIR), is a random copolymer of isobutylene with 1-2 mol% isoprene (Figure 1.1) which was first synthesized in 1937 at the Standard Oil Development Company. IIR is synthesized from 2-methylpropene (isobutylene) and 2-methyl-1,3-butadiene (isoprene) through a complex cationic copolymerization mechanism, resulting mainly in trans-1,4-addition of isoprene to isobutylene in a head-to-tail configuration.¹ The small amount of isoprene provides reactive unsaturation for vulcanization, while the isobutylene provides superior weathering, ozone resistance and oxidative stability.²

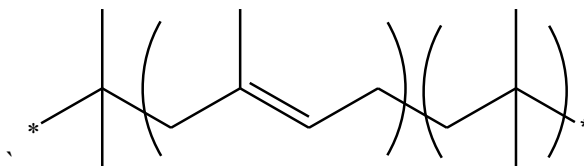


Figure 1.1: Structure of Poly(isobutylene-co-isoprene)

The first application for butyl rubber was inner tubes in automobile tires due to its excellent air retention. However, for the purpose of tire inner liners, the limited functionality resulted in slow vulcanization rates compared to highly unsaturated elastomers used in the tire treads and wall. Since all components of the tire must be cured under identical conditions and at comparable rates, IIR alone is unsuitable for inner liners. Halogenation of butyl rubber (Section 1.2) can be employed to improve

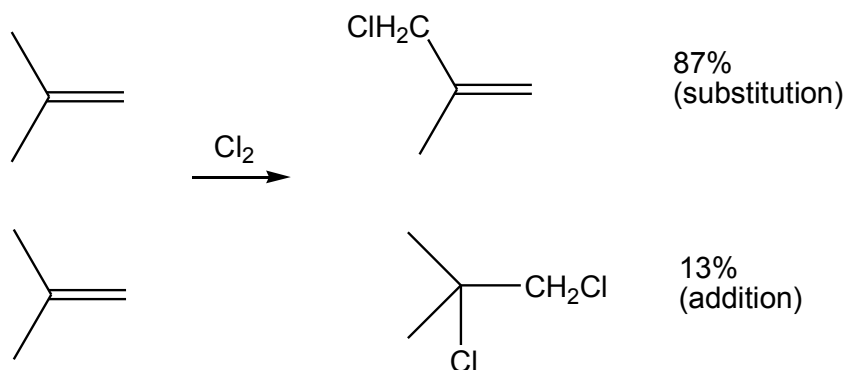
vulcanization rates and compatibility with other elastomers³, making it suitable for inner liner applications.

1.2 Halogenation of Butyl Rubber

The isoprene mer in butyl rubber can be modified through halogenation to form a reactive allylic halide functionality which greatly improves its reactivity towards sulfur and other nucleophiles. Currently, chlorinated (CIIR) and brominated (BIIR) butyl rubbers are commercially available. Industrial halogenation of butyl rubber is done in a hexanes solution using either elemental chlorine or bromine. Reactions between olefins and the halogens have been investigated extensively and can be applied to the study of butyl rubber halogenation.

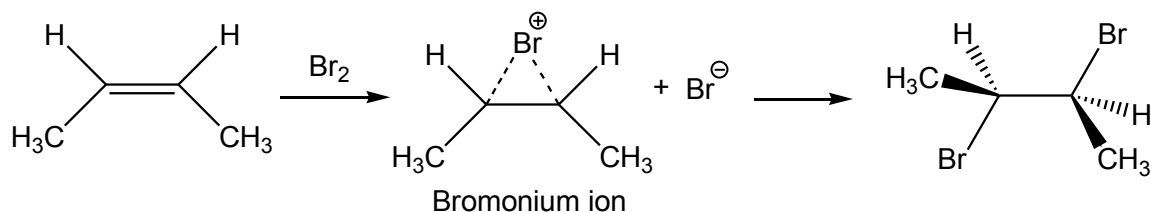
It has been demonstrated that there is competition between an ionic and free-radical reaction pathway during halogenation of olefins.⁴ Reactions of trans-2-butene with chlorine showed both the radical and ionic pathways favoured the addition product. The chlorination of isobutylene proceeded through an ionic pathway which predominately formed the substitution product (Scheme 1.1). The radical mechanism was not observed for isobutylene under normal conditions, however when induced it was shown to favour the addition product. Poustma et al.⁴ demonstrated that halogenations of branched and highly substituted alkenes proceed through an ionic pathway which favours substitution products.

Scheme 1.1: Chlorination of Isobutylene



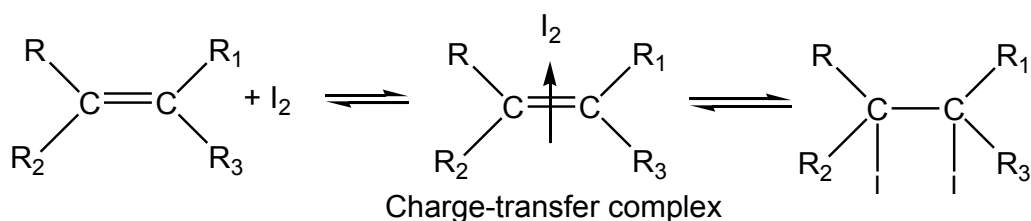
It is well known that bromination of alkenes occurs through an electrophilic addition mechanism to form dibromides. Bromination of *cis*-2-butene through an ionic mechanism resulted in a higher amount of the anti addition product, indicating rotation around the carbon-carbon double bond is inhibited during halogenation. The lack of rotation was best described by a halonium ion (bromonium ion for bromination) intermediate structure, as shown in Scheme 1.2 for the bromination of *cis*-2-butene.^{5,6} Further work to support the halonium ion intermediate structure was done by Brown et al.⁷, using X-ray diffraction to characterize the bromonium and iodonium ions of triflate salts of adamantylideneadamantane (Ad=Ad). They determined the bond length and angles associated with these halonium ions.

Scheme 1.2: Bromination of *cis*-2-butene



Studies on the mechanism for the addition of iodine to alkenes are limited, however it is well known that iodination is reversible and therefore does not reach full conversion.⁸ Since both bromination and chlorination addition reactions go to completion, it has been questioned whether iodination proceeds through a different mechanism. Though Brown et al.⁷ characterized an iodonium ion of triflate salts of adamantylideneadamantane (Ad=Ad), evidence for this intermediate structure in the iodination of most alkenes has not been well established. An alternative mechanism has been proposed, in which a charge-transfer complex (Scheme 1.3) is an intermediate present during the addition of iodide across the double bond.⁹

Scheme 1.3: Proposed mechanism for iodination of alkenes

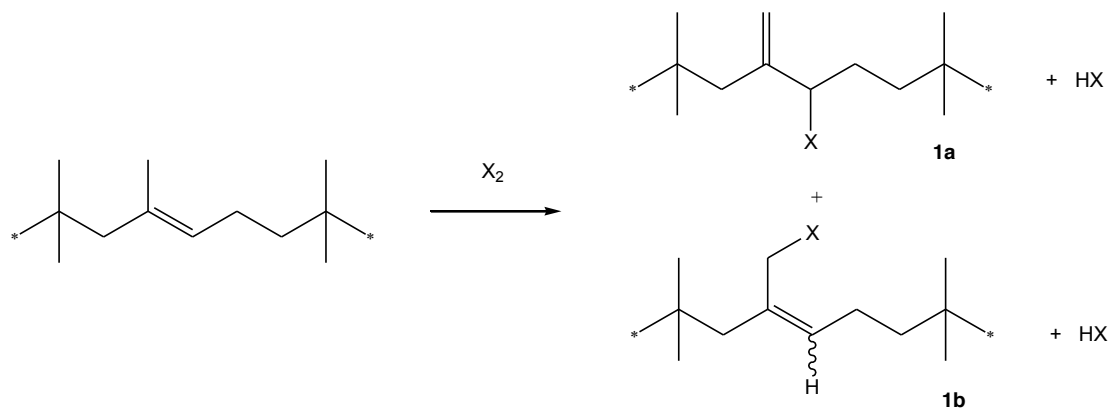


Mechanistic halogenation studies with small molecule alkenes provide insight into the reactivity of each halogen with butyl rubber, however to further understand butyl rubber halogenations it is important to study the final product distributions. Characterizing this product distribution can be difficult. Nuclear Magnetic Resonance spectroscopy (NMR) on long chained polymers dissolved in solution leads to broadened peaks as they have extended relaxation times, resulting in poor peak resolution. The low olefin concentrations (1-2 mol%) in butyl rubber make it especially difficult to characterize using NMR and other standard techniques, such as mass spectrometry. The best way to resolve this issue is to use a model compound, which is a small molecule that imitates the

structure of the reactive functionality in the polymer. Vukov used 2,2,4,8,8-pentamethyl-4-nonene (PMN) as an appropriate compound to model the isoprene functionality of butyl rubber and its reactivity with elemental bromine and chlorine to determine product distributions.¹⁰

Vukov¹⁰ characterized the reaction products for both bromination and chlorination of PMN and IIR, determining that both yielded only substitution products (Scheme 1.4). Bromination resulted in 90% conversion to the *exo*-methylene bromide (**1a**, where X=Br) isomer, the kinetically favoured product and 10% conversion to the (*E,Z*)-*endo*-bromomethyl (**1b**, where X=Br) isomers, the thermodynamically favoured product. Chlorination resulted in the *exo*-methylene (**1a**, where X=Cl) isomer exclusively. Vukov attributes the selectivity for substitution products to the steric effects imposed by the bulky *t*-butyl group β to double bond. The structural effects of these bulky groups prevent nucleophilic attack of the free halide ions on the halonium ion intermediate while encouraging deprotonation at the sterically less hindered methyl site, alpha to the double bond.

Scheme 1.4: Halogenation of Butyl Rubber



1.3 Vulcanization of Halogenated Butyl Rubber

Vulcanization of IIR and its halogenated derivatives extends their utility to many practical applications, including tire inner liners. Since rubber is a viscoelastic material, when left uncured it undergoes irreversible deformation when a stress is applied. Vulcanization reduces this plasticity while increasing elasticity through the formation of cross-links between polymer chains. The formation of a covalent molecular network within the material improves the mechanical and physical properties making it suitable for use in a variety of industrial applications. Sulphur is commonly used to form crosslinks between polymer chains (Figure 1.2), however other curing agents are often used for the vulcanization of polymers.

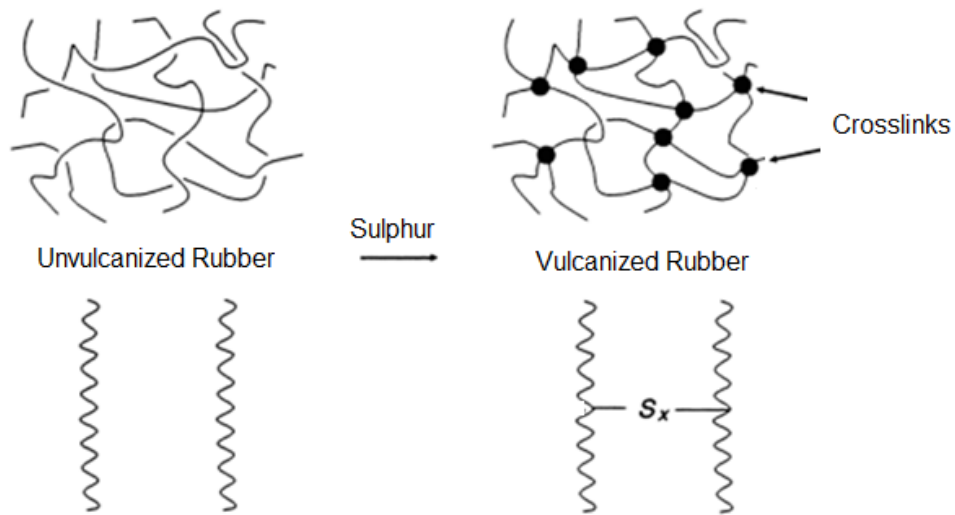


Figure 1.2: Crosslink network developed through vulcanization with sulphur¹¹

An oscillating biconical disc rheometer is commonly used to measure the extent of vulcanization of a material. The polymer and curative formula are mixed together and a

sample of the mixture is placed between two biconical plates which are set to a controlled temperature. The bottom plate rotates at a set frequency while the top plate remains stationary creating a sinusoidal strain on the sample. Continuous measurements of the torque that the sample imposes on the top plate are used to quantify the stress response to this strain. Using the shear stress data, the storage (G') and the loss (G'') components of the dynamic modulus (G^*) can be calculated. It is important to note that the dynamic modulus of viscoelastic materials includes both storage and loss contributions to capture the elastic and viscous behavior. The storage modulus represents the elastic component of the material and is a measurement of stored energy, whereas the loss modulus represents the viscous component of the material and is a measurement of the energy lost as heat. The relationship between dynamic modulus (G^*) and the storage modulus (G') and loss modulus (G'') is:

$$G^* = G' + iG'' \quad (1)$$

where, i is a complex number

A standard vulcanization curve showing storage modulus as a function of time contains three distinct regions (Figure 1.3). The first phase of the cure is the delay or scorch time, which is representative of the materials resistance to premature curing. This induction period is important because it not only allows for complete mixing of the polymer with the curative and other additives but it also provides time for the material to flow into the mold and take shape into the desired product. The second stage of the vulcanization process is the cure phase. During the cure phase, crosslinks must be formed rapidly to

build material strength but also reduce the potential for degradation products which can occur at the high temperatures used for vulcanization. The final stage of the vulcanization is dependent on how well the extent of cure is controlled and the stability of the crosslink network. The ideal outcome is the modulus will reach a stable plateau, however if the modulus continues to increase (marching modulus) or starts to decline (cure reversion) it represents instability in the crosslink network.

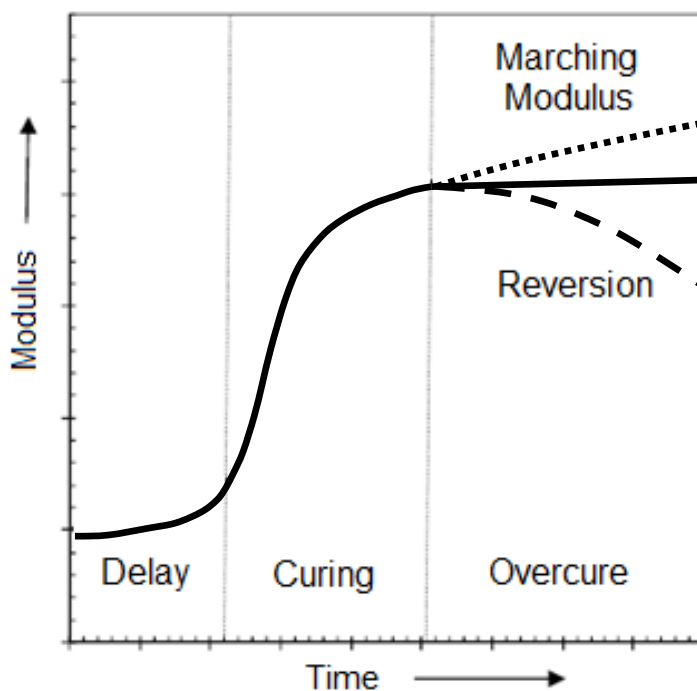


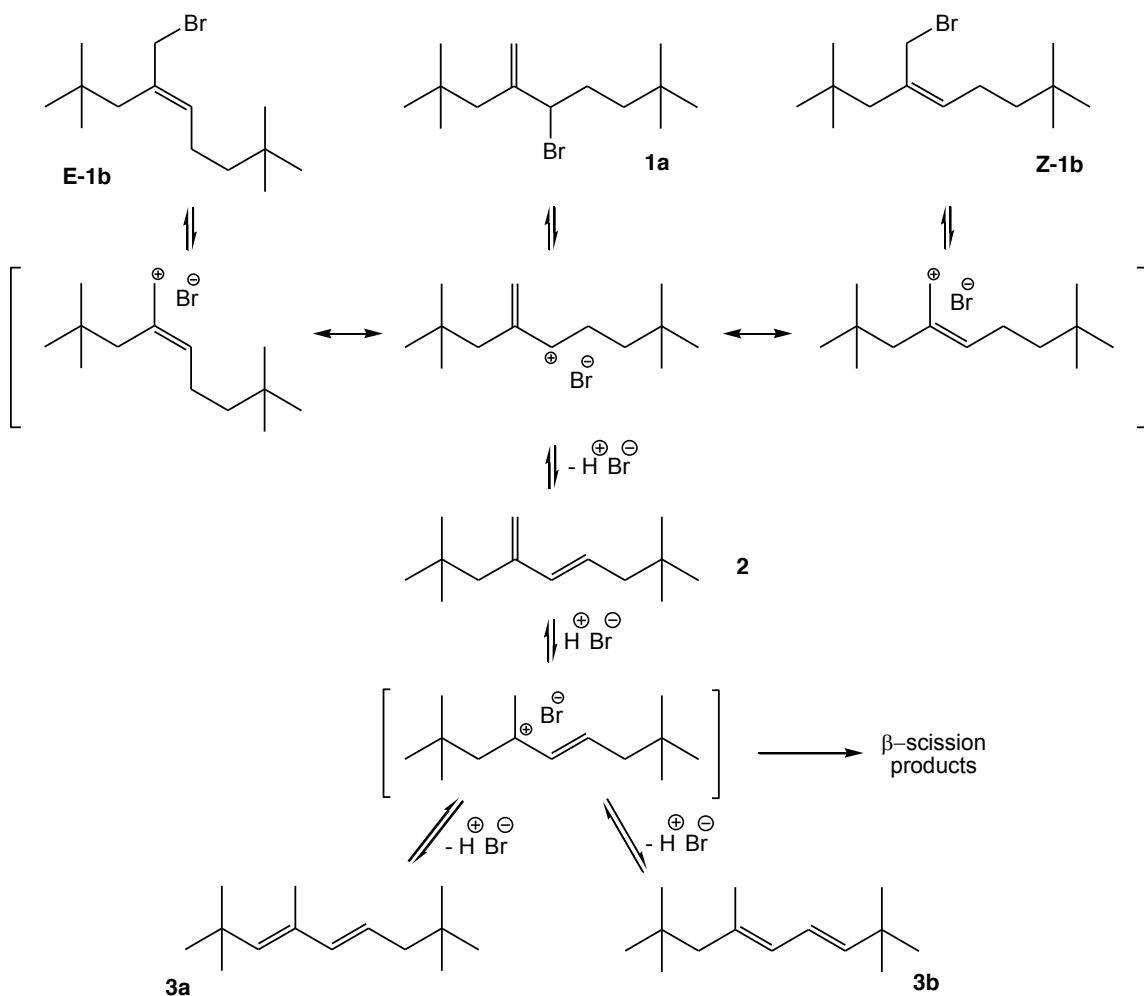
Figure 1.3: Standard Vulcanization Curve for rubber-based compounds¹²

1.4 Thermal Stability of Allylic Bromide Isomers

Halogenation of butyl rubber increases its reactivity towards sulphur, improving vulcanization rates and making it ideal for use in tire inner liner formulations. Since standard vulcanization temperatures can reach as high as 170°C, Parent et al.¹³ studied

the stability of BIIR and BPMN at these temperatures. Their studies showed that heating BPMN and BIIR promoted isomerization of *exo*-methylene bromide (Exo-Br) isomer to the thermodynamically more stable (*E,Z*)-*endo*-bromomethyl (r-BIIR) isomer. At increased temperatures, isomerisation occurs concurrently with dehydrobromination resulting in HBr and conjugated dienes formation (Scheme 1.5). Dehydrobromination can also reduce the molecular weight of the polymer through β -scission of allyl cation intermediates.

Scheme 1.5: Thermal Stability of the allylic bromide in BPMN/BIIR¹³

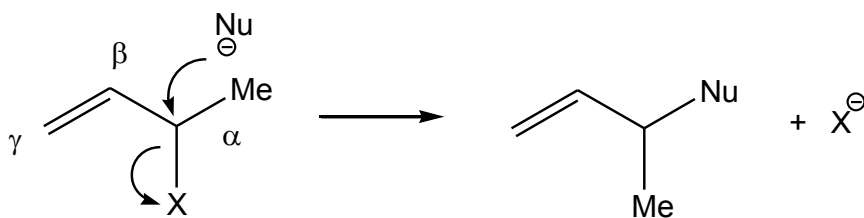


Parent et al.¹³ heated BPMN with an initial ratio of 55:45 *exo*-methylene (**1a**) to (*E,Z*)-*endo*-bromomethyl (**1b**) to 145°C and established a final isomer ratio of 15:85 in one minute. Accompanying the isomerisation was the formation of conjugated diene structures (**2,3a,3b**) and HBr as a result of dehydrobromination. Although debromination of BIIR saw similar products as BPMN, it contains epoxides and calcium stearate which act as acid scavengers. These acid scavengers stabilize BIIR by neutralizing evolved HBr and limiting further dehydrobromination which reduces the formation of conjugated dienes as well as reducing the potential for molecular weight reduction through β -scission.

1.5 Nucleophilic Substitution Reactions of Allylic Halides

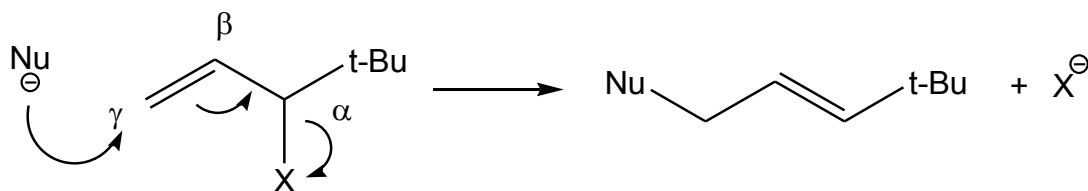
The allylic halide functionality found in halogenated butyl rubber increases its reactivity towards a wide range of nucleophiles and provides a foundation for further derivatization of butyl rubber. The chemical and physical properties of butyl rubber can be manipulated and exploited through the use of different nucleophiles. Allylic halides generally undergo bimolecular nucleophilic substitution (S_N2) and abnormal S_N2 (S_N2') reactions. The S_N2 mechanism results in inversion of stereochemistry at the α -carbon where substitution occurs and loss of the halide group (Scheme 1.6). In the case of the S_N2' mechanism, the substitution occurs at the γ -carbon with migration of the double bond (Scheme 1.7).¹⁴

Scheme 1.6: S_N2 Substitution Reaction Mechanism



When the methyl group on the α-carbon (Scheme 1.6) is replaced with a bulky t-butyl group (Scheme 1.7) it introduces steric hindrance at this site.¹⁵ The γ-carbon of the double bond is less sterically hindered and thus becomes the easier site for the nucleophile to attack.

Scheme 1.7: S_N2' Substitution Reaction Mechanism



As stated earlier, bromination of commercial grades of IIR results in mainly the *exo*-methylene bromide (**1a**) isomer formation. Nucleophilic attack on this isomer at the α-carbon is inhibited by four methyl groups causing steric hindrance towards large nucleophiles.¹⁵ The γ-carbon is more accessible than the α-carbon, therefore the S_N2' mechanism is likely preferred. This affects the final product distribution, limiting the amount of S_N2 products which leave the double bond in the *exo*-methylene formation.

Two important factors affecting the reaction rate of nucleophilic substitution of halobutyl rubber are leaving group ability of the displaced halide and nucleophilicity of the

nucleophile. Since chloride is a worse leaving group than bromide, it will likely reduce the reactivity of chlorobutyl rubber towards nucleophiles that may otherwise be successful for bromobutyl rubber.

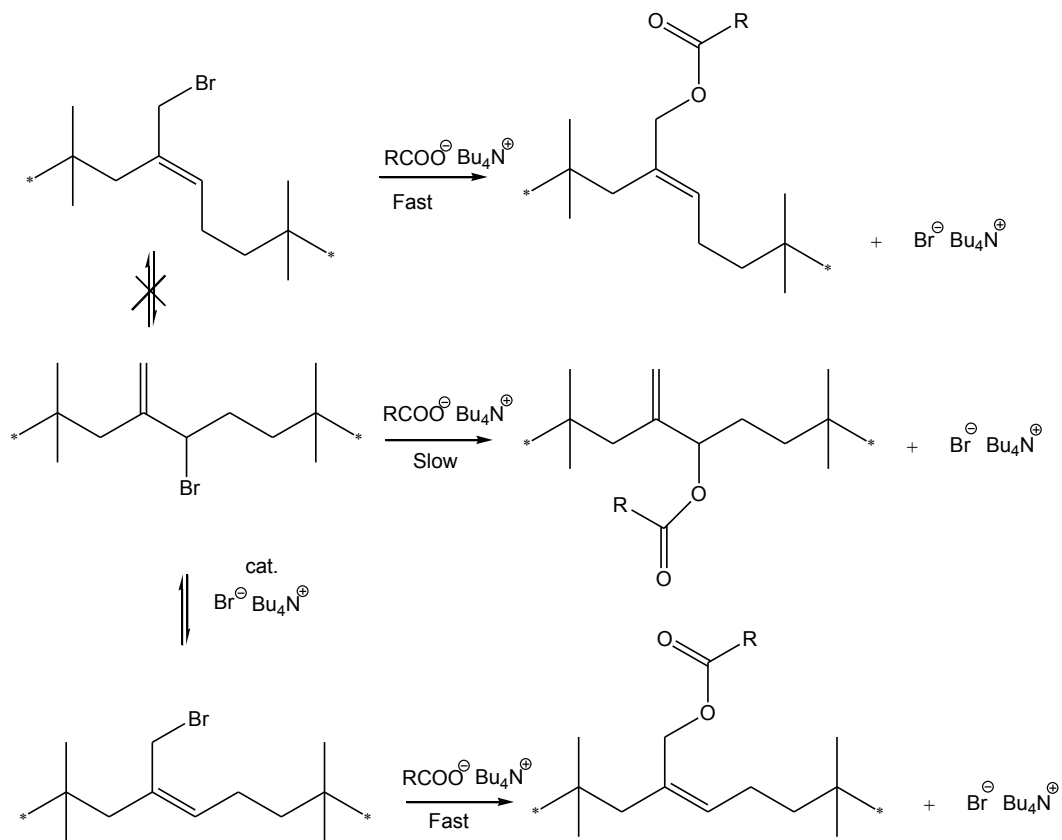
The reactivity of carboxylate nucleophiles with allylic halide functionally in BIIR has been of interest to prepare butyl rubber derivatives containing pendant polymerizable functionality.¹⁶

Gullien-Castellanos et al.¹⁷ reacted BIIR in solution of toluene with soluble quaternary ammonium carboxylate salt at 85°C to gain insight into the reaction mechanism. The studies specifically looked at the dependence of esterification rates and product distributions on both nucleophile concentrations and initial allylic bromide isomer distributions.

Gullien-Castellanos¹⁷ demonstrated the superior reactivity of (*E,Z*)-*endo*-bromomethyl isomers over the *Exo*-Br isomer, as BIIR samples with a higher quantity of (*E,Z*)-*endo*-bromomethyl isomers reacted faster than samples with a higher proportion of *Exo*-Br. By observing the starting allylic bromide isomer distribution and final allylic ester isomer distributions of each reaction, they determined that allylic ester formation proceeds through an S_N2 mechanism, converting the *exo*-allylic bromide into its corresponding *exo*-ester product and (*E,Z*)-*endo*-bromomethyl isomer into its corresponding allylic ester (Scheme 1.8). It was also shown that a side product of the substitution reaction, a quaternary ammonium bromide salt, promoted *Exo*-Br isomerization to (*E,Z*)-*endo*-

bromomethyl isomers through an S_N2' mechanism. Parent et al.¹⁸ expanded on this research showing that this type of esterification follows auto-accelerating kinetics. During esterification tetra-*n*-butylammonium bromide (TBAB) is released which catalyzes allylic bromide rearrangement from the less reactive Exo-Br isomer to the more reactive (*Z*)-*endo*-bromomethyl isomer (Scheme 1.8).

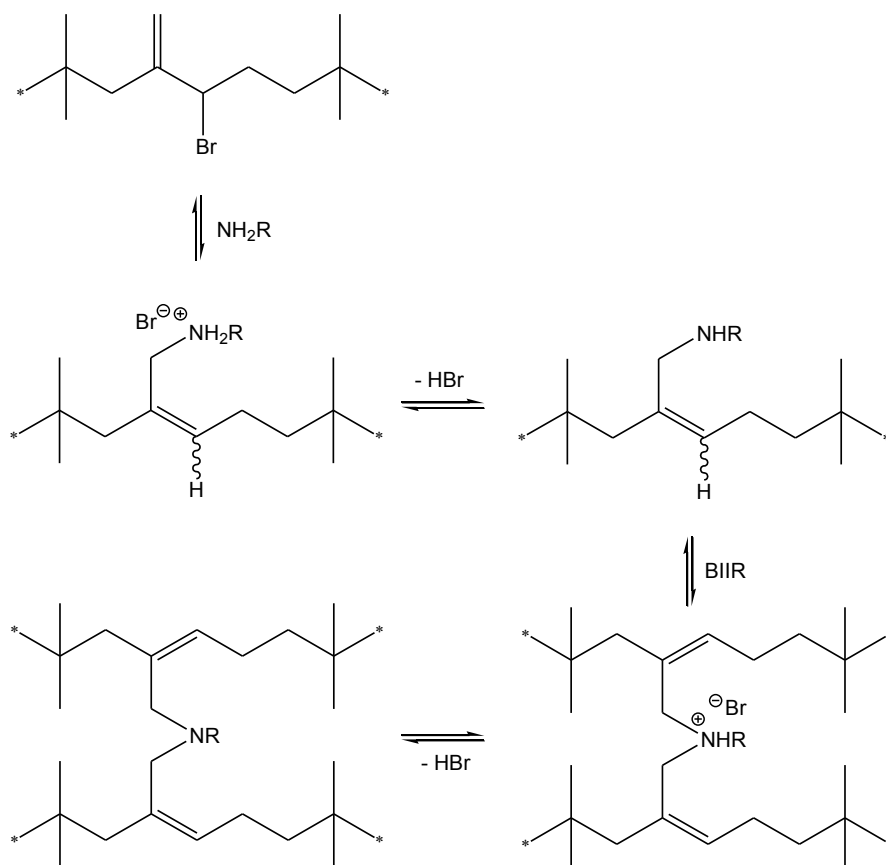
Scheme 1.8: General kinetic scheme for BIIR and Bu₄NAc reactions^{17,18}



Solvent-free nucleophilic substitution reactions of BIIR with primary, secondary and tertiary amines have been studied¹⁹ to expand on BIIR reactivity with various nucleophiles. BIIR with octylamine was found to undergo N-alkylation twice to produce

bis-N-alkylation products (Scheme 1.9), indicating that primary amines have the ability to produce a covalent crosslinked network when reacted with BIIR.

Scheme 1.9: Bis-N-Alkylation of BIIR¹⁹

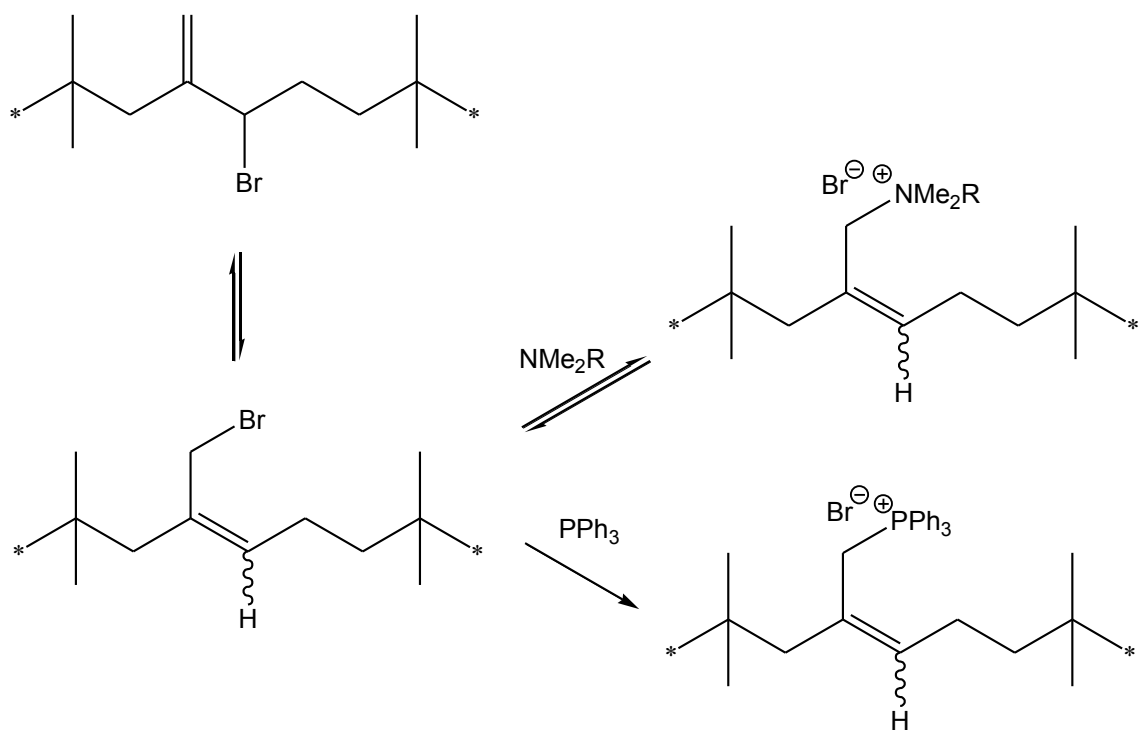


BIIR was reacted with N-methyloctadecylamine and N,N-dimethyloctylamine (DMOA), secondary and tertiary amines respectively, at 140°C showing N-alkylation, rearrangement (**1a to 1b**) and dehydrobromination products. The N-alkylation products were exclusively (*E,Z*)-*endo*-substitution derivatives, showing no signs of any *exo*-methylene substitution products. Previous studies have observed that N-alkylation reactions of allylic halides with dimethylamine and trimethylamine are selective for $\text{S}_{\text{N}}2'$

displacement products.²⁰ In the study of the N-alkylation of BIIR however, rapid isomerization from Exo-Br isomer to (*E,Z*)-*endo*-bromomethyl isomers cannot be disregarded, making it difficult to assign S_N2 or S_N2' mechanism. The presence of conjugated diene structures (**2**, **3a**, **3b**) during the N-alkylation of BIIR at 140°C indicated that dehydrobromination was a competing reaction pathway. N-alkylation of BIIR was found to be reversible, with the final product distribution being controlled by a thermodynamic equilibrium.

Tertiary amines as nucleophiles for BIIR substitution reactions were studied further by Parent et al.²¹ through investigations of the formation of ammonium and phosphonium based ionomers from BIIR using DMOA and triphenylphosphine (Scheme 1.10). When triphenylphosphine was used as a nucleophile to undergo substitution reaction with BIIR it resulted exclusively in the (*E,Z*)-*endo*-phosphonium salt derivatives, which was consistent with their ammonium counterpart. However, differences in rate of formation were observed, as ionomers derived from triphenylphosphine with BIIR showed much slower reaction rates than those derived from DMOA with BIIR. Although triphenylphosphine was found to be less nucleophilic than DMOA, the reaction did proceed irreversibly.

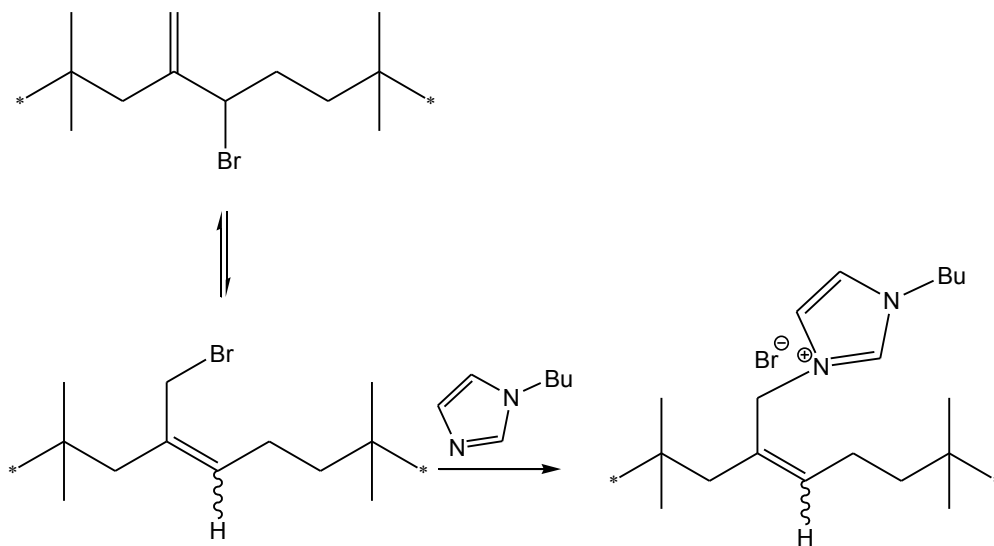
Scheme 1.10: Phosphonium bromide and Ammonium bromide derivatives of BIIR



Substitution of the allylic bromide functionality with ammonium or phosphonium salts²¹ produces an elastomeric ionomer with unique properties. Ion-pair aggregation of the phosphonium and ammonium salts leads to an ionic network which restricts the polymer chain mobility. Both phosphonium bromide and quaternary ammonium bromide ionomers showed an increase in storage modulus (G') directly proportion to the extent of alkylation indicating aggregation of the ionic group. Ionomers can be considered a labile analogue of covalently vulcanized materials, as the ionic network can be broken down by separation of the ionic groups.²² These elastomeric ionomers were determined to have comparable mechanical properties to ZnO-cured vulcanizates. It was also concluded ionomers containing ammonium salts have instability issues due to the reversibility of the N-alkylation.

Further studies of elastomeric ionomers derived from BIIR lead to the investigation of 1-butylimidazole as a potential nucleophile for N-alkylation of BIIR (Scheme 1.11)²³. Following the trend of previously studied ionomers, the reaction of 1-butylimidazole with BIIR produced exclusively the (*E,Z*)-*endo*-substitution products. The reaction was shown to be irreversible unlike previously studied N-alkylations of BIIR which showed product instability due to reversibility of the reaction. The product stability and the versatility of the imidazole ring functionality provide a foundation for investigating derivatives of BIIR with various functional groups.

Scheme 1.11: N-alkylation of BIIR with N-butylimidazole



1.6 Research Objectives

The isoprene mer in butyl rubber can be modified through halogenation to form reactive allylic halide functionality. This functionality can undergo nucleophilic substitution with

various nucleophiles to produce different derivatives of butyl rubber. An important factor affecting the reaction rate of nucleophilic substitution of halobutyl rubber is leaving group ability of the displaced halide. The main objective of this research is to investigate the effect of leaving group ability on the stability and reactivity of halobutyl rubbers. The goal was approached through the following steps:

1. Produce comparable iodobutyl, bromobutyl and chlorobutyl rubber derivatives.
2. Compare the rate of dehydrohalogenation of iodo-, bromo- and chloro-butyl rubbers.
3. Put iodobutyl rubber reactivity into context by comparing it to chloro- and bromo-butyl rubber using a variety of nucleophiles.

The initial focus of the research is to produce comparable products of iodobutyl, bromobutyl and chlorobutyl rubbers. Each material will ideally have similar microstructures, with comparable *exo*-methylene halide:(*E*)-*endo*-halomethyl:(*Z*)-*endo*-halomethyl isomer ratios. The amount of conjugated dienes in these materials should be limited as it could influence future reaction results.

1.7 Thesis Outline

As discussed previously, the objective of this thesis is to investigate the effects of leaving group ability and microstructure of the reactivity of halobutyl rubber. Chapter 2 discusses

the preparation and characterization of each halobutyl rubber derivative. In Chapter 3, the halobutyl rubber derivatives are compared in terms of their thermal stability and reactivity towards nucleophilic substitution. Finally, conclusions and recommendations for future work are summarized in Chapter 4.

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Chapter 2. Halobutyl Rubbers: Microstructure and Model Compounds

2.1 Introduction

The isoprene unit in butyl rubber can be modified through halogenation to form an allylic halide functionality, which greatly improves its reactivity towards various nucleophiles. Currently, chlorinated and brominated butyl rubbers are commercially available. The formation of fluorinated and iodinated butyl rubbers could provide a series of halogenated rubbers with different halide leaving groups. Since an important feature of nucleophilic substitution reactions with halogenated butyl rubber is leaving group ability of the displaced halide, these materials would provide a basis for determining the effect of leaving group ability on the stability and reactivity on halobutyl rubbers.

The fluorination of butyl rubber through conventional methods would likely be unsuccessful as elemental fluorine reacts violently with alkenes to give a variety of products resulting from degradation of the carbon chain. While other derivatives of fluorine, such as xenon difluoride¹, have been shown to successfully add fluorine to alkenes, fluoride is an extremely poor leaving group. If fluorinated butyl rubber were prepared, it would be very stable in the presence of various nucleophiles, hence, it was omitted from this study.

It is well known that the addition of iodine to alkenes is reversible², making the iodination of butyl rubber through conventional methods difficult due to product instability. Alternative iodinating agents, such as N-iodosuccinimide, have been

investigated; however, each was unsuccessful at producing an iodinated butyl rubber derivative.³ Studies into the nucleophilic catalyzed bromide displacement of BIIR using tetra-*n*-butylammonium iodide (TBAI)⁴ led to the discovery of an allylic iodide intermediate. It was determined that when excess TBAI was reacted with BIIR, the final product contained mainly (*E,Z*)-*endo*-allylic iodide functionality. Further to this research, 2,2,4,8,8-pentamethyl-4-nonene (PMN), a suitable model compound for the isoprene functionality in butyl rubber, was brominated then reacted with excess sodium iodide (NaI) to produce a final product that contained only the (*E,Z*)-allylic iodide functionality. The conclusions from these studies noted that while iodinated butyl rubber is a viable product, it likely contains only (*E,Z*)-*endo*-iodomethyl (r-IIIR) isomers as opposed to the *exo*-methylene iodide (Exo-I) isomer.

Since synthesis of iodobutyl rubber only results in (*E,Z*)-*endo*-iodomethyl functionality, this section will focus on producing brominated and chlorinated butyl rubbers with (*E,Z*)-*endo*-halomethyl functionality. The objective will be to produce iodobutyl, bromobutyl and chlorobutyl rubbers with comparable microstructures with the intent of subsequently using these materials for comparative assessment of reactivities.

2.2 Experimental

2.2.1 Materials

The following chemicals were used as received: Bromobutyl 2030 (LANXESS Inc., $M_n \approx 400\,000$ g/mol, allylic bromide content ≈ 0.15 mmol/g.), Chlorobutyl 1240 (LANXESS

Inc, allylic chloride content \approx 0.21mmol/g), tetra-*n*-butylammonium bromide (TBAB, 99%, Sigma-Aldrich), tetra-*n*-butylammonium iodide (TBAI, 98%, Sigma-Aldrich), tetra-*n*-butylammonium chloride (TBAC, Sigma-Aldrich), zinc stearate (Sigma-Aldrich). 2,2,4,8,8-Pentamethyl-4-nonene (PMN) and brominated 2,2,4,8,8-pentamethyl-4-nonene (BPMN) were prepared as previously described.⁵ All reactions were performed in a round bottom flask equipped with a Teflon® magnetic stir bar and under reflux, unless otherwise specified.

2.2.2 Isomerization of bromobutyl rubber

Isomerization using TBAB in THF

A solution of commercial BIIR (5 g) and TBAB (5 eq., 1.2 g) in THF (51 ml) was heated for 4 h at 70°C. The product was recovered by precipitation from acetone and dried under vacuum at room temperature. Samples withdrawn at regular intervals were characterized by ¹H NMR (CDCl₃) spectroscopy with integration to an accuracy of \pm 5%: δ 5.01 (*Exo*-Br, =CHH, 1H, s); δ 4.11 (*E*-BrMe, =C-CH₂-Br, 2H, s), δ 4.09 (*Z*-BrMe, =C-CH₂-Br, 2H, s).

Isomerization using TBAB in toluene

A solution of commercial BIIR (2 g) and TBAB (0.1 eq., 0.01 g) was heated in toluene (20 ml) for 4 h at 85°C. The product was recovered by precipitation from acetone and dried under vacuum at room temperature. Samples withdrawn at regular intervals were characterized by ¹H NMR (CDCl₃) spectroscopy with integration to an accuracy of \pm 5%:

δ 5.01 (*Exo*-Br, =CHH, 1H, s); δ 4.11 (*E*-BrMe, =C-CH₂-Br, 2H, s), δ 4.09 (*Z*-BrMe, =C-CH₂-Br, 2H, s).

Isomerization using Zinc Stearate

A solution of commercial BIIR (2 g) and zinc stearate (1 eq, 0.20 g) was heated in toluene (20 ml) for 4 h at 85°C. The product was recovered by precipitation from acetone and dried under vacuum at room temperature. Samples withdrawn at regular intervals were characterized by ¹H NMR (CDCl₃) spectroscopy with integration to an accuracy of \pm 5%: δ 5.01 (*Exo*-Br, =CHH, 1H, s); δ 4.11 (*E*-BrMe, =C-CH₂-Br, 2H, s), δ 4.09 (*Z*-BrMe, =C-CH₂-Br, 2H, s).

Isomerization of BIIR alone

A solution of commercial BIIR (2 g) was heated in toluene (20 ml) for 4 h at 85°C. The product was recovered by precipitation from acetone and dried under vacuum at room temperature. Samples withdrawn at regular intervals were characterized by ¹H NMR (CDCl₃) spectroscopy with integration to an accuracy of \pm 5%: δ 5.01 (*Exo*-Br, =CHH, 1H, s); δ 4.11 (*E*-BrMe, =C-CH₂-Br, 2H, s), δ 4.09 (*Z*-BrMe, =C-CH₂-Br, 2H, s).

2.2.3 Isomerization of chlorobutyl rubber

Isomerization using TBAC

A solution of commercial CIIR (2 g) and TBAC (0.1 eq., 0.01 g) was heated in toluene (20 ml) for 4 h at 85°C. The product was recovered by precipitation from acetone and dried under vacuum at room temperature. Samples withdrawn at regular intervals were

characterized by ^1H NMR (CDCl_3) spectroscopy with integration to an accuracy of $\pm 5\%$: δ 5.01 (*Exo*-Cl, =**CHH**, 1H, s); δ 4.10 (*E*-ClMe, =C-**CH₂**-Cl, 2H, s), δ 4.11 (*Z*-ClMe, =C-**CH₂**-Cl, 2H, s).

Isomerization using Zinc Stearate

A solution of commercial CIIR (2 g) and zinc stearate (1 eq., 0.21 g) was heated in toluene (20 ml) for 4 h at 85°C. The product was recovered by precipitation from acetone and dried under vacuum at room temperature. Samples withdrawn at regular intervals were characterized by ^1H NMR (CDCl_3) spectroscopy with integration to an accuracy of $\pm 5\%$: δ 5.01 (*Exo*-Cl, =**CHH**, 1H, s); δ 4.10 (*E*-ClMe, =C-**CH₂**-Cl, 2H, s), δ 4.11 (*Z*-ClMe, =C-**CH₂**-Cl, 2H, s).

Isomerization of CIIR alone

A solution of commercial CIIR (2 g) was heated in toluene (20 ml) for 4 h at 85°C. The product was recovered by precipitation from acetone and dried under vacuum at room temperature. Samples withdrawn at regular intervals were characterized by ^1H NMR (CDCl_3) spectroscopy with integration to an accuracy of $\pm 5\%$: δ 5.01 (*Exo*-Cl, =**CHH**, 1H, s); δ 4.10 (*E*-ClMe, =C-**CH₂**-Cl, 2H, s), δ 4.11 (*Z*-ClMe, =C-**CH₂**-Cl, 2H, s).

2.2.4 Halide Displacement of rearranged bromobutyl rubber

Formation of r-IIIR in solution

A solution of r-BIIR (5 g) and TBAI (10 eq., 2.7 g) in THF (51 ml) was heated for 30 min at 70°C. The product was recovered by precipitation from acetone and dried under

vacuum at room temperature. Samples withdrawn at regular intervals were characterized by ^1H NMR (CDCl_3) spectroscopy with integration to an accuracy of $\pm 5\%$: δ 5.01 (*Exo*-Br, =**CHH**, 1H, s); δ 4.09 (*Z*-BrMe, =C-**CH₂**-Br, 2H, s); *E*-BrMe: δ 4.08 (=C-**CH₂**-I, 2H, s), δ 5.81 (**CH**=C-CH₂-I, 2H, t); *Z*-IMe: δ 3.99 (=C-**CH₂**-I, 2H, s), δ 5.35 (**CH**=C-CH₂-I, 2H, t).

Formation of r-CIIR in solution

A solution of r-BIIR (5 g) and TBAC (5 eq., 1.1 g) in THF (51 ml) was heated for 2 h at 70°C. The product was recovered by precipitation from acetone and dried under vacuum at room temperature. Samples withdrawn at regular intervals were characterized by ^1H NMR (CDCl_3) spectroscopy with integration to an accuracy of $\pm 5\%$: δ 5.01 (*Exo*-Cl, =**CHH**, 1H, s); δ 4.10 (*E*-ClMe, =C-**CH₂**-Cl, 2H, s), δ 4.11 (*Z*-ClMe, =C-**CH₂**-Cl, 2H, s).

2.2.5 Halogenation of 2,2,4,8,8-pentamethyl-4-nonene

Iodination of 2,2,4,8,8-pentamethyl-4-nonene

A solution of BPMN (3 mg, 0.011 mmol) in toluene-*d*₈ was heated to 85°C for 2 days. Excess NaI (5 mg, 0.033 mmol) was added to the solution of isomerized BPMN in deuterated acetone ($(\text{CD}_3)_2\text{CO}$) (0.5 ml,) was heated to 45°C for 3 h to give the desired iodinated derivative. ^1H NMR (CDCl_3): *E*-IMe: δ 4.07 (=C-**CH₂**-I, 2H, s), δ 5.83 (-**CH**=C-CH₂-I, 2H, t); *Z*-IMe: δ 3.97 (=C-**CH₂**-I, 2H, s), δ 5.33 (-**CH**=C-CH₂-I, 2H, t). MS analysis: required mass for $\text{C}_{14}\text{H}_{27}\text{I}$ is 322.1158 *m/e*, found 322.1161 *m/e* (TOF MS EI+). This procedure has been adapted from previous work⁴

Chlorination of 2,2,4,8,8-pentamethyl-4-nonene

A solution of PMN (0.1 g, 0.510 mmol) in CH_2Cl_2 (2.5 mL) was chilled under N_2 before the addition of 1,3-dichloro-5,5-dimethylhydantoin (0.06 g, 0.305 mmol) and 2,6-di-*tert*-butylcresol (0.0013 g, 0.006 mmol). The mixture was stirred in the dark for 105 min at 0°C under N_2 . After concentration *in vacuo* at the workup temperature, chilled hexanes (10 mL) were added, and the mixture was filtered and finally concentrated *in vacuo* to yield to a clear yellow liquid. ^1H NMR revealed *exo*-methylene allylic chloride. An aliquot of this liquid was dissolved in toluene- d_8 and heated to 85°C for 2 weeks. The toluene- d_8 was allowed to evaporate over 2 days and the remaining liquid was dissolved in CDCl_3 for ^1H NMR analysis. δ 5.01 (*Exo*-Cl, =**CHH**, 1H, s); δ 4.11 (*E*-ClMe, =C-**CH₂**-Cl, 2H, s), δ 4.10 (*Z*-ClMe, =C-**CH₂**-Cl, 2H, s). MS analysis: required mass for $\text{C}_{14}\text{H}_{27}\text{Cl}$ is 230.1801 *m/e*, found 230.1812 *m/e* (TOF MS EI+).

2.2.6 Instrumentation and Analysis

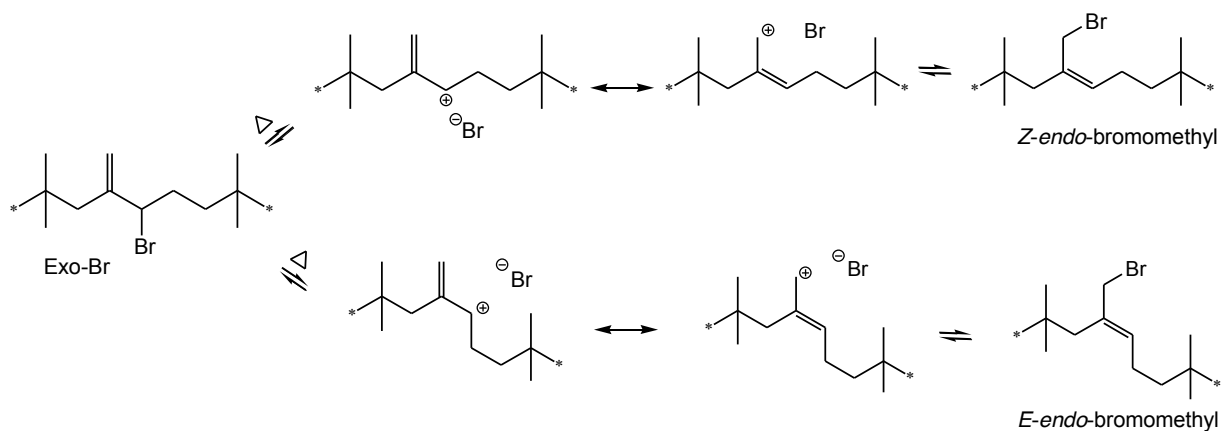
^1H -NMR spectra were acquired in CDCl_3 (^1H 7.26 ppm) at 400 MHz on a Bruker Avance-400 spectrometer, at 500 MHz on a Bruker Avance-500 spectrometer or at 600 MHz on a Bruker Avance-600 spectrometer. All chemical shifts were referenced to deuterated chloroform (CDCl_3).

2.3 Results and Discussion

2.3.1 Dynamics of allyl bromide isomerization

The dominant product from the bromination of butyl rubber is the kinetically more favoured *exo*-methylene allylic bromide isomer, which can undergo rearrangement to a more thermodynamically stable product containing (*E,Z*)-*endo*-bromomethyl functionality.⁶ Isomerization can proceed through two different mechanisms depending on the reaction conditions. The first of these reaction pathways proceeds through allyl bromide ionization, followed by recombination with rearrangement (Scheme 2.1). The reaction kinetics for this isomerization pathway are sensitive to temperature and the presence of a Lewis acid. Isomerization is also shown to proceed through S_N2' pathway, as simultaneous bond-making and bond-breaking occurs when a nucleophilic catalyst is used to promote isomerization (Scheme 2.2)⁷.

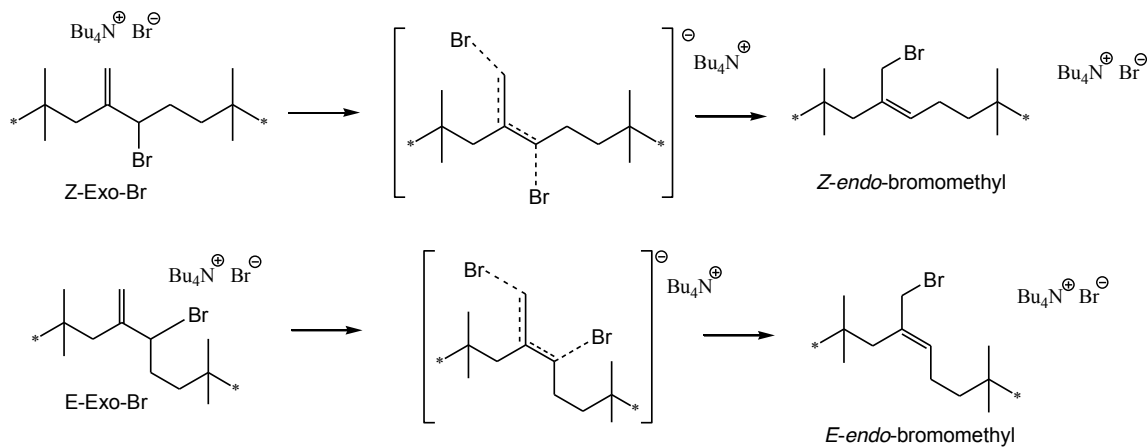
Scheme 2.1: Isomerization of *exo*-methylene allyl bromide to (*E,Z*)-*endo*-bromomethyl isomers through an allyl cation pathway



It has been shown that iodobutyl rubber containing the *exo*-methylene iodide isomer is not a stable product; therefore, it was essential to isomerize commercial BIIR to

accurately compare the nucleophilic substitution and dehydrohalogenation reaction dynamics of these materials. With the objective of completely isomerizing commercial BIIR from the *exo*-methylene bromide isomer to an equal ratio of (*E,Z*)-*endo*-bromomethyl isomers, the reaction dynamics and allylic bromide isomer distribution of three potential isomerization methods were compared. Figure 2.1 shows the progression of allyl bromide isomer distribution for toluene solutions containing 10 wt% BIIR at 85°C for isomerization reactions containing no catalyst, a Lewis acid catalyst and a nucleophilic catalyst.

Scheme 2.2: Isomerization of *exo*-methylene bromide isomers to (*E,Z*)-*endo*-bromomethyl isomers through an S_N2' pathway



Uncatalyzed isomerization reactions of BIIR showed little reactivity in 5 hours at 85°C (Figure 2.1 a). Increasing the temperature improves the reaction kinetics however higher temperatures promote allyl cation deprotonation to form conjugated dienes and HBr. Lewis acids have also been shown to improve isomerization rates as they increase BIIR

susceptibility to ionization.^{4,8} When 1 molar equivalence of zinc stearate was used as a catalyst for BIIR isomerization at 85°C, a marked increase in reactivity was seen (Figure 2.1 b). Since uncatalyzed and Lewis acid catalyzed isomerizations proceed through an allyl cation pathway (Scheme 2.1), bond rotation in the allyl cation intermediate leads to equal distributions of (*E*)-*endo*-bromomethyl and (*Z*)-*endo*-bromomethyl isomers. The disadvantage associated with this isomerization pathway is the limited temperature range as the allyl cation intermediate is prone to deprotonation at high temperature, forming unwanted byproducts.⁵ Lewis acids are also incompatible with most nucleophiles, which therefore limits the range of nucleophilic substitution reactions that can follow isomerization with zinc stearate.

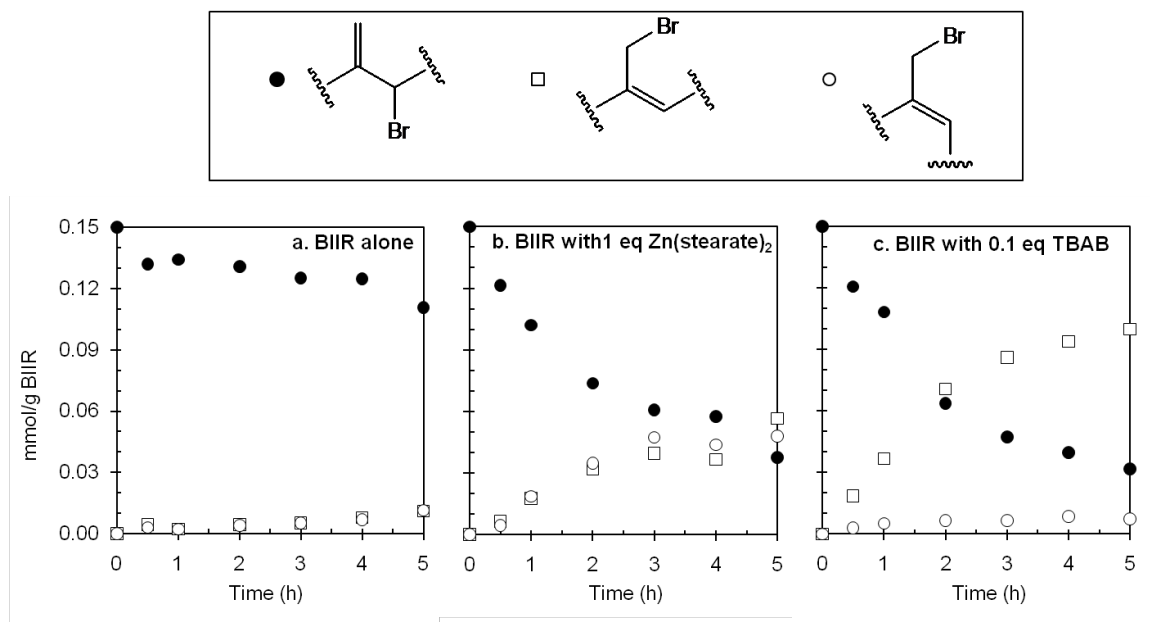


Figure 2.1: Allylic bromide isomerization; a. Uncatalyzed; b. Lewis acid catalyzed; c. TBAB catalyzed (10 wt% BIIR in toluene, 85°C)

Tetra-*n*-butylammonium bromide (TBAB) has been shown to catalyze allylic bromide rearrangement, with bromide acting as a nucleophilic catalyst.^{7,8,9} When 0.1 molar equivalents of TBAB (Figure 2.1c) were used to catalyze the isomerization in a toluene solution at 85°C, a 75:25 ratio of (*E,Z*)-*endo*-bromomethyl:Exo-Br isomers was produced in 5 hours. The reaction was selective for the (*Z*)-*endo*-bromomethyl isomer due to the nature of commercial BIIR, in which the *exo* allylic bromide has a preference for specific conformation (Figure 2.2, **Z-Exo-Br**). The S_N2' mechanism is advantageous because it is not prone to dehydrobromination as it does not proceed through an allyl cation intermediate.

The final allylic bromide isomer ratios for isomerization reactions containing no catalyst, a Lewis acid catalyst and a nucleophilic catalyst are compared and summarized in Table 2.1. Residual Exo-Br was unavoidable in all three methods as it is presumed an equilibrium between reactants and products exists. Zinc stearate catalyzed isomerization produced the most ideal allylic bromide ratio for further comparison to chloro- and iodo-butyl rubber; however, its incompatibility with most nucleophiles makes this method unsuitable for this study. TBAB catalyzed isomerization does not reach our ideal allylic bromide ratio, but TBAB is easily removed from the final product eliminating unwanted interactions with nucleophiles used in future analysis.

Table 2.1: Final Allylic Bromide Distributions^a

Isomerization Method	Final Allylic Bromide Ratio Exo-Br : (<i>E</i>)-endo-bromomethyl : (<i>Z</i>)-endo- bromomethyl
BIIR Alone	80 : 10 : 10
1 eq Zn(stearate) ₂	25 : 35 : 40
0.1 eq TBAB	15 : 10 : 75

a. 10 wt% BIIR in toluene; 85°C; 4 hrs

Commercial BIIR was completely isomerized to accurately compare the nucleophilic substitution and dehydrohalogenation dynamics with iodobutyl rubber. TBAB catalyzed isomerization provided the most suitable material as it produced an Exo-Br:(*E,Z*)-endo-bromomethyl ratio of 15:85 and residual catalyst was easily removed.

2.3.2 Dynamics of allyl chloride isomerization

It was necessary to isomerize CIIR to accurately compare its nucleophilic substitution and dehydrohalogenation reaction dynamics with iodobutyl rubber. The same approach for studying the isomerization of commercial BIIR was applied to commercial CIIR. Figure 2.2 shows the progression of allyl chloride isomer distribution for toluene solutions containing 10 wt% CIIR at 85°C for isomerization reactions containing no catalyst, a Lewis acid catalyst and a nucleophilic catalyst.

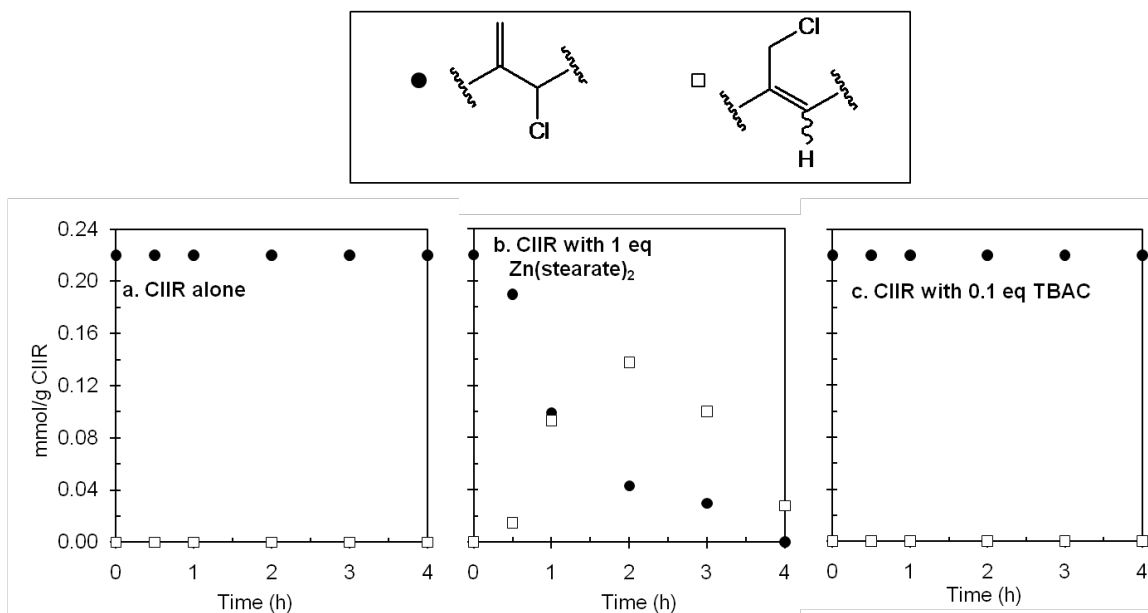


Figure 2.2: Allylic chloride isomerization; a. Uncatalyzed; b. Lewis acid catalyzed; c. TBAC catalyzed (10 wt% CIIR in toluene, 85°C)

Uncatalyzed isomerization reactions of CIIR showed no reactivity in 4 hours at 85°C (Figure 2.2 a). BIIR under the same conditions (Figure 2.1 a) resulted in an Exo-Br:(*E,Z*)-*endo*-bromomethyl isomer ratio of 90:10 in 4 hours. The lack of reactivity of CIIR towards uncatalyzed isomerization can be explained by the leaving group ability of chloride relative to bromide. Chloride is a less favourable leaving group than bromide as it is more basic and thus, a less stable anion. In addition, the C-Cl bond has a higher bond dissociation energy than the C-Br bond, making it more difficult to break. Therefore, the bromide in BIIR is more likely to leave, allowing for the formation of the allyl cation intermediate (Scheme 2.1), than the chloride ion in CIIR.

When 1 molar equivalent of zinc stearate was used as a catalyst for CIIR isomerization at 85°C, the reaction proceeded to an *exo*-methylene chloride:(*E,Z*)-*endo*-chloromethyl isomer ratio of 25:75 in 2 hours (Figure 2.2 b). After 2 hours, the allylic chloride functionality decreased as the material endured rapid dehydrohalogenation producing conjugated dienes and HCl. This is indicative of the allyl cation mechanism (Scheme 2.1). It should be noted that in the presence of a Lewis acid, CIIR was observed to be more susceptible to allyl cation deprotonation during isomerization than BIIR. This increased vulnerability can be explained by the difference in basicity of the chloride and bromide anions. Due to its increased basicity, the chloride anion is more likely to deprotonate the allyl cation intermediate than the bromide anion, which increases the rate of dehydrohalogenation.

The effect of 0.1 molar equivalence of TBAC on a 10 wt% toluene solution of CIIR at 85°C is demonstrated in Figure 2.2 c. In the presence of a nucleophilic catalyst, CIIR showed no reactivity over 4 hours. This observation is of particular interest because it shows that CIIR, in the presence of a chloride catalyst, does not have the capability of isomerizing through an S_N2' mechanism (see Scheme 2.2). Alternatively, BIIR in the presence of a bromide catalyst is perfectly capable of the isomerization reaction. To better understand the reactivity of CIIR, it was reacted with 5 equivalents TBAB in a THF solution. The dynamics (Appendix A1) showed CIIR had a lack of reactivity towards isomerization and halide exchange even with an excess of bromide. This can be explained by the leaving group ability of bromide and chloride. As stated earlier, bromide

is a better leaving group than chloride making BIIR more reactive towards nucleophilic catalyzed isomerization.

Commercial CIIR must be completely isomerized to accurately compare the nucleophilic substitution and dehydrohalogenation dynamics to iodobutyl rubber. All three methods (uncatalyzed, Lewis acid catalyzed and nucleophile catalyzed) were unsuitable for this purpose. Isomerization reactions containing no catalyst or a nucleophilic catalyst showed no rearrangement from the *exo*-methylene chloride (Exo-Cl) isomer to the (E,Z)-*endo*-chloromethyl isomer (r-CIIR). The zinc stearate catalyzed isomerization successfully isomerized CIIR however, the reaction was sensitive to dehydrochlorination and resulted in unwanted byproducts. As stated earlier, another factor which makes isomerization with zinc stearate unsuitable for this research is its incompatibility with a variety of nucleophiles.

2.3.3 Dynamics of nucleophilic catalyzed halide displacement

Nucleophilic catalyzed bromide displacement of BIIR has been shown previously through the use of tetra-*n*-butylammonium iodide (TBAI).⁴ The iodide in TBAI acts as a nucleophile to displace bromide, producing an allylic iodide intermediate which is more reactive than the allylic bromide functionality. This increased reactivity has been shown to improve BIIR reactivity towards nucleophilic substitution. It has also been shown that an excess of TBAI could be reacted with BIIR to form a final product containing mainly allylic iodide functionality.

Bromide displacement in BIIR with other halides such as chloride and iodide was studied further with the objective of producing butyl rubber with (*E,Z*)-*endo*-chloromethyl (r-CIIR) and (*E,Z*)-*endo*iodomethyl (r-IIIR) functionality. Figure 2.3 illustrates the dynamics of reactions conducted with different halide nucleophiles and/or initial allylic bromide isomer distributions. In these plots, allyl group concentrations are expressed as mmoles of functionality per gram of elastomer (mmol/g-XIIR), and tetra-*n*-butylammonium chloride (TBAC) and tetra-*n*-butylammonium iodide (TBAI) concentrations are listed as molar equivalents relative to the 0.15 mmol/g of allylic bromide within BIIR.

The experiments illustrated in Figure 2.3a and 2.3 c summarize the reactions of 10 wt% THF solutions of commercial BIIR that contain 90:10 ratio of Exo-Br:(*E,Z*)-*endo*-bromomethyl, with excess TBAI and TBAC, respectively. As expected, the reaction with TBAI saw an evolution of both (*E,Z*)-*endo*-bromomethyl isomers, the product of BIIR isomerization, and (*E,Z*)-*endo*-iodomethyl, the product of halide exchange, within the first 120 minutes. After 120 minutes, much of the (*E,Z*)-*endo*-bromomethyl functionality was consumed to form additional (*E,Z*)-*endo*-iodomethyl functionality. When excess TBAC was employed (Figure 2.3 c), two particularly interesting outcomes were observed. Firstly, while TBAI initially catalyzed BIIR isomerization, TBAC showed no isomerization activity, consuming all the allylic bromide functionality in 180 minutes. The second notable feature was the evolution of both *exo*-allylic chloride and (*E,Z*)-*endo*-

allylic chloride functionality resulting in a final Exo-Cl:(*E,Z*)-endo-chloromethyl isomer ratio of 70:30.

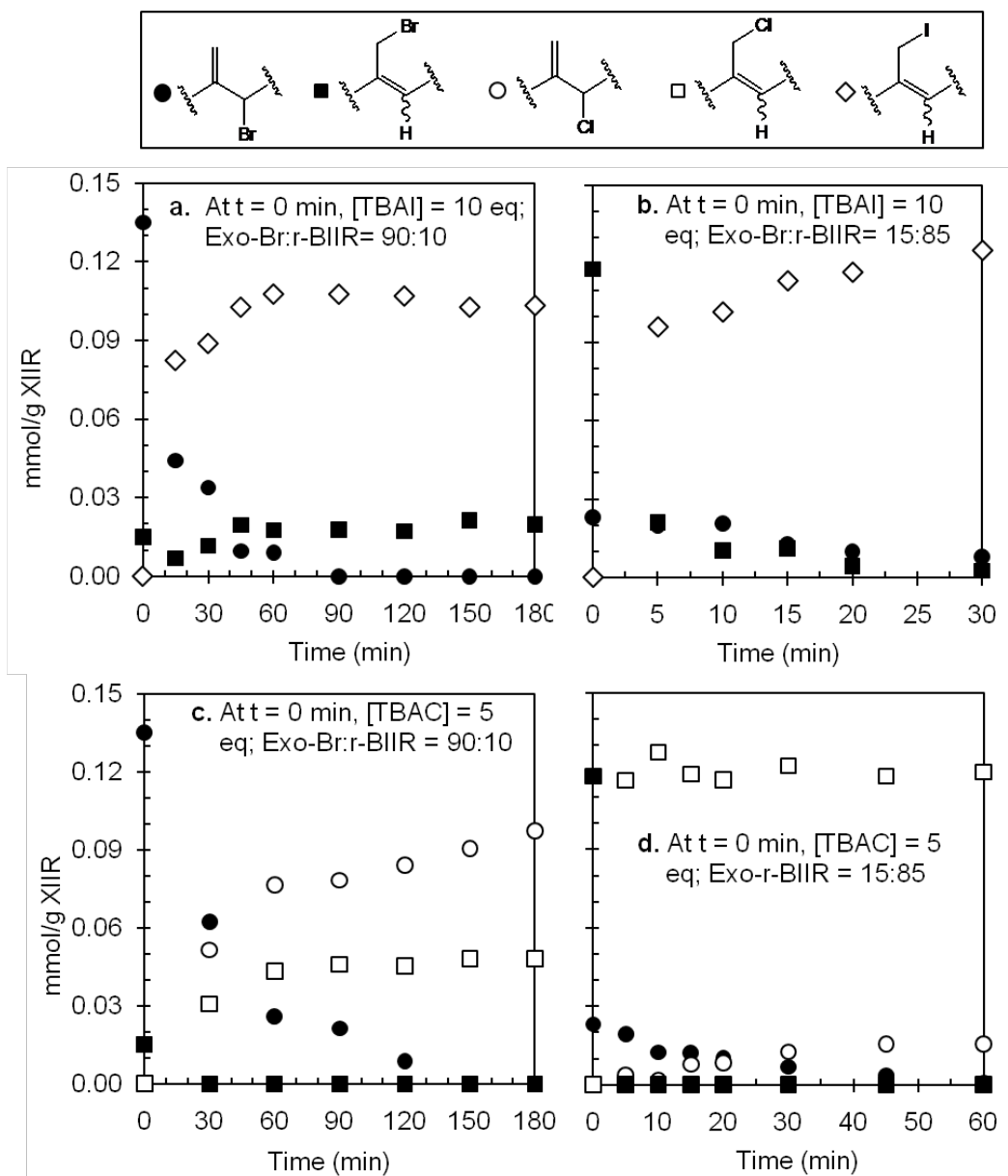


Figure 2.3: Dynamics of halide displacement of BIIR; a. BIIR as received - 10 eq TBAI; b. TBAB isomerized BIIR – 10 eq TBAI; c. BIIR as received – 5 eq TBAC; d. TBAB isomerized BIIR – 5 eq TBAC; (10 wt% BIIR in THF solutions, 70°C)

Insight was gained from starting materials containing different ratios of allylic bromide isomers. Figures 2.3 b and 2.3 d summarize the reactions of 10 wt% THF solutions of BIIR that contain 15:85 ratio of Exo-Br:(*E,Z*)-*endo*-bromomethyl, with excess TBAI and TBAC. With considerably less Exo-Br functionality, TBAI consumed most of the (*E,Z*)-*endo*-bromomethyl functionality forming (*E,Z*)-*endo*-iodomethyl functionality within 5 minutes of reacting. The small amount of Exo-Br functionality was consumed at a slower rate as it was isomerized first to (*E,Z*)-*endo*-bromomethyl isomers which were subsequently replaced with (*E,Z*)-*endo*-iodomethyl functionality. The instability of the r-IIIR shows after 30 minutes as it undergoes reversible halide displacement with TBAB to reform r-BIIR. Consumption of the (*E,Z*)-*endo*-bromomethyl functionality was immediate with an excess of TBAC (Figure 2.3d), while Exo-Br functionality was consumed over a period of 60 minutes. The product isolated after 60 minutes contained a 15:85 Exo-Cl:(*E,Z*)-*endo*-chloromethyl isomer ratio.

Halogenated butyl rubbers, including r-CIIR and r-IIIR, were produced through reactions of isomerized BIIR with TBAC and TBAI. The study provided insight into the mechanism employed by both TBAI and TBAC in the presence of halogenated butyl rubber. It has been determined that TBAI is likely to react through an S_N2' mechanism, showing similarities to TBAB. The preference for *exo*-allylic chloride functionality when reacted with commercial BIIR, as well as the inability for TBAC to isomerize CIIR established that chloride, as a nucleophile, is likely to react through an S_N2 mechanism.

The behaviour demonstrated by TBAC is more comparable to the previously studied tetra-*n*-butylammonium acetate (TBAAc).⁴

2.3.4 Halobutyl Rubber characterization

Explicit characterization of the microstructure found in each halobutyl rubber was achieved through the preparation of iodinated, brominated and chlorinated 2,2,4,8,8-pentamethyl-4-nonene. ¹H-NMR spectra of the three halogenated model compounds are compared in Figure 2.4.

Previous studies on chlorinated 2,2,4,8,8-pentamethyl-4-nonene (CPMN)^{6,10} and brominated 2,2,4,8,8-pentamethyl-4-nonene (BPMN)^{5,6,10} have focused on the exo-methylene halide isomer. To attain a full representation of the microstructure, CPMN was allowed to isomerize in deuterated toluene solution at 85°C. Figure 2.4c contains the ¹H-NMR spectrum of the product recovered after CPMN was heated for 2 weeks. CPMN isomerization is recognized by the evolution of two singlets at δ 4.10 and δ 4.11, which correspond to (*E*)-*endo*-chloromethyl and (*Z*)-*endo*-chloromethyl isomers, respectively. Figure 2.4b contains the ¹H-NMR spectrum of the product recovered after BPMN was heated for 24 hours in a deuterated toluene solution. Exo-Br isomerization to (*E*)-*endo*-bromomethyl and (*Z*)-*endo*-bromomethyl can be seen by the development of two singlets at δ 4.05 and δ 4.09, respectively. Iodinated 2,2,4,8,8-pentamethyl-4-nonene (IPMN) was produced through halide exchange of BPMN using sodium iodide (NaI) in deuterated acetone (Figure 2.4a) through a Finkelstein type reaction mechanism, as previously

prepared. The *exo*-methylene iodide isomer is not present in IPMN however the singlets at δ 3.95 and δ 4.05 correspond to the (*E*)-*endo*-iodomethyl and (*Z*)-*endo*-iodomethyl isomers, respectively.

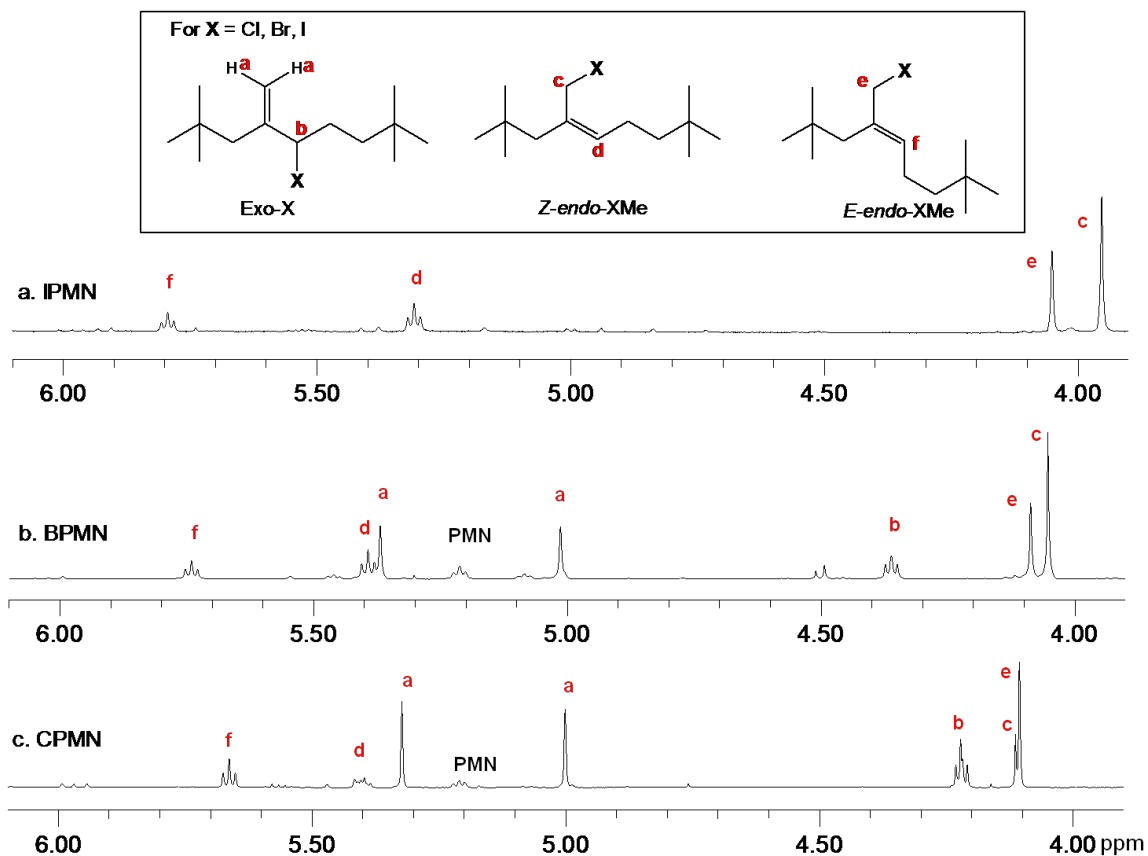


Figure 2.4: Downfield region of $^1\text{H-NMR}$ spectra (CDCl_3) a. Iodinated model compound; b. Brominated model compound; c. Chlorinated model compound

Methods for producing brominated, chlorinated and iodinated derivatives of butyl rubber derivatives with (*E,Z*)-*endo*-halomethyl functionality have been developed and $^1\text{H-NMR}$ spectra of the three compounds are compared in Figure 2.5. To assure the halobutyl

rubbers have comparable microstructures, each polymer system was tested for consistency to its appropriate model compound.

To maintain consistency between preparation methods, all reactions were heated to 70°C in a THF solution containing 10 wt% of either commercial BIIR or TBAB isomerized BIIR. Isomerized BIIR was prepared from heating commercial BIIR with 5 molar equivalence of TBAB for 4 hours, as evident from the spectrum provided in Figure 2.5b. Figure 2.5a contains the ¹H-NMR spectrum of the product recovered from heating TBAB isomerized BIIR for 30 minutes in the presence of 10 molar equivalence TBAI. Finally, the ¹H-NMR spectrum in Figure 2.5c depicts the product recovered from heating TBAB isomerized BIIR in the presence of 5 molar equivalence TBAC for 2 hours.

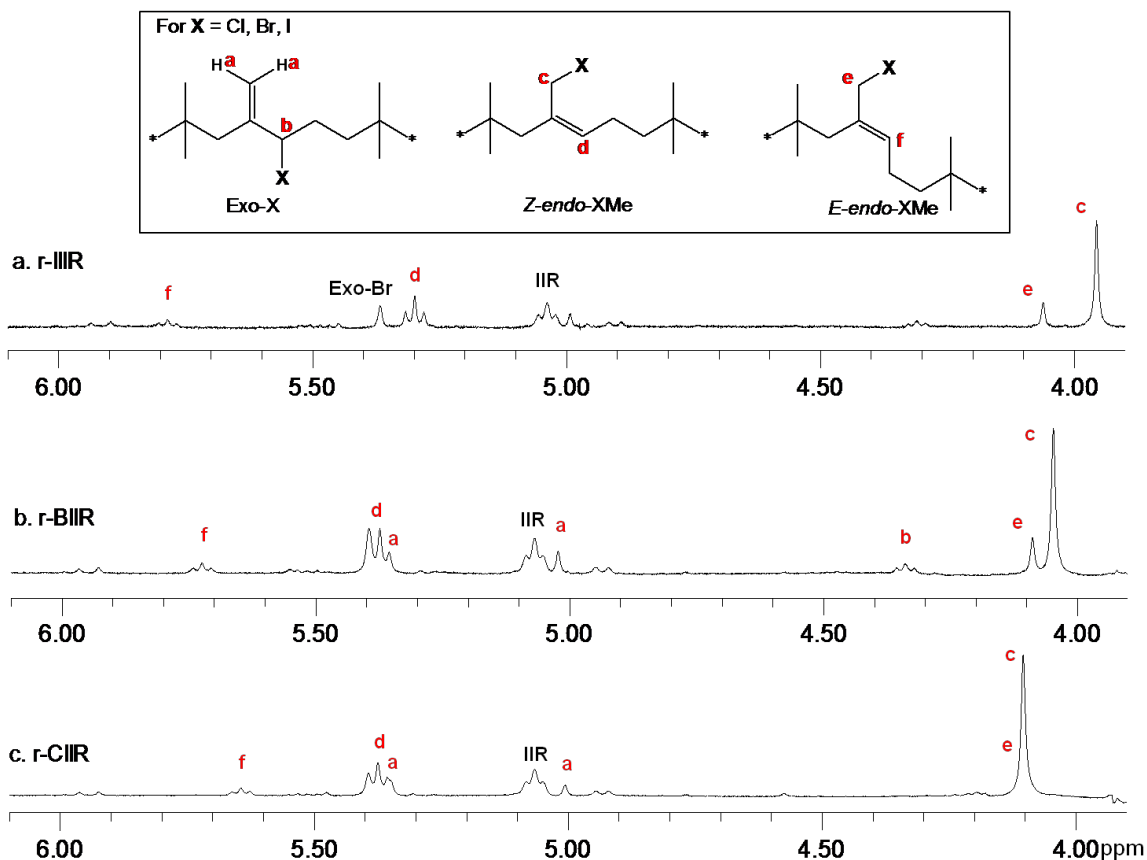


Figure 2.5: Downfield region of $^1\text{H-NMR}$ spectra (CDCl_3) a. Rearranged iodinated butyl rubber; b. Rearranged brominated butyl rubber; c. Rearranged chlorinated butyl rubber

Since the different allylic halide isomer peaks in the halobutyl rubber $^1\text{H-NMR}$ spectra can be accurately identified through use of the model compound spectra, the final allylic halide isomer ratios for each compound were determined and compared in Table 2.2. The final allylic halide ratios for each polymer are comparable and are suitable for further investigation of their dehydrohalogenation and nucleophilic substitution reaction dynamics. It should be noted that residual Exo-Br isomer was unavoidable during the isomerization of commercial BIIR and this is carried through to IIR and CIIR samples. The formation of a small amount of conjugated dienes in both IIR and CIIR is also

inevitable, as both are exposed to sustained heat for a sufficient period of time to initiate dehydrohalogenation.

Table 2.2: Final distribution of allylic halide and conjugated dienes for Halobutyl Rubbers

Compound	Final Allylic Halide Ratio
	Exo-X : (Z)-endo-halomethyl : (E)-endo-halomethyl : Conjugated Dienes
r-IIR ^a	00 : 60 : 20 : 10*
r-BIIR ^b	15 : 75 : 10 : 00
r-CIIR ^c	10 : 70 : 10 : 10

*Remaining 10% is contributed to residual Exo-Br and (Z)-endo-bromomethyl isomers.

a. 10 wt% r-BIIR in THF; 10 eq TBAI; 70^oC; 30mins

b. 10 wt% BIIR in THF; 5 eq TBAB; 70^oC; 4hrs

c. 10 wt% r-BIIR in THF; 5 eq TBAC; 70^oC; 2hrs

2.4 Conclusion

Brominated, chlorinated and iodinated derivatives of butyl rubber derivatives with (E,Z)-allylic halide functionality have been prepared and characterized with the assistance of model compounds. The amount of *exo*-methylene halide, (Z)-endo-halomethyl, and (E)-endo-halomethyl isomers for each material were determined through ¹H-NMR analysis and found to be comparable, and will be used for further investigations of the dehydrohalogenation and nucleophilic substitution reaction dynamics.

The isomerization of BIIR and CIIR were studied in the presence of no catalyst, a Lewis acid catalyst and a nucleophilic catalyst. Both BIIR and CIIR readily isomerized when

catalyzed with $\text{Zn}(\text{stearate})_2$, a Lewis acid, through allyl cation mechanism. While BIIR was shown to isomerize through an $\text{S}_{\text{N}}2'$ mechanism, CIIR showed no reactivity toward this mechanism.

Halide exchange of BIIR and r-BIIR with excess TBAC and TBAI salts were studied. An excess of TBAI was shown to undergo halide exchange with both BIIR and r-BIIR to produce a polymer containing mainly (*E,Z*)-*endo*-iodomethyl isomers. BIIR with an excess of TBAC reacted to give a product containing both the *exo*-methylene chloride and (*E,Z*)-*endo*-chloromethyl isomers. The *exo*-methylene chloride isomer was produced along with TBAB through halide exchange of chloride with BIIR. It is likely the TBAB would isomerize BIIR to its (*E,Z*)-*endo*-bromomethyl isomers, which subsequently undergo halide exchange with TBAC to produce (*E,Z*)-*endo*-chloromethyl isomers. An excess of TBAC with r-BIIR reacted to form a product that contained mainly the (*E,Z*)-*endo*-chloromethyl isomers, through halide exchange.

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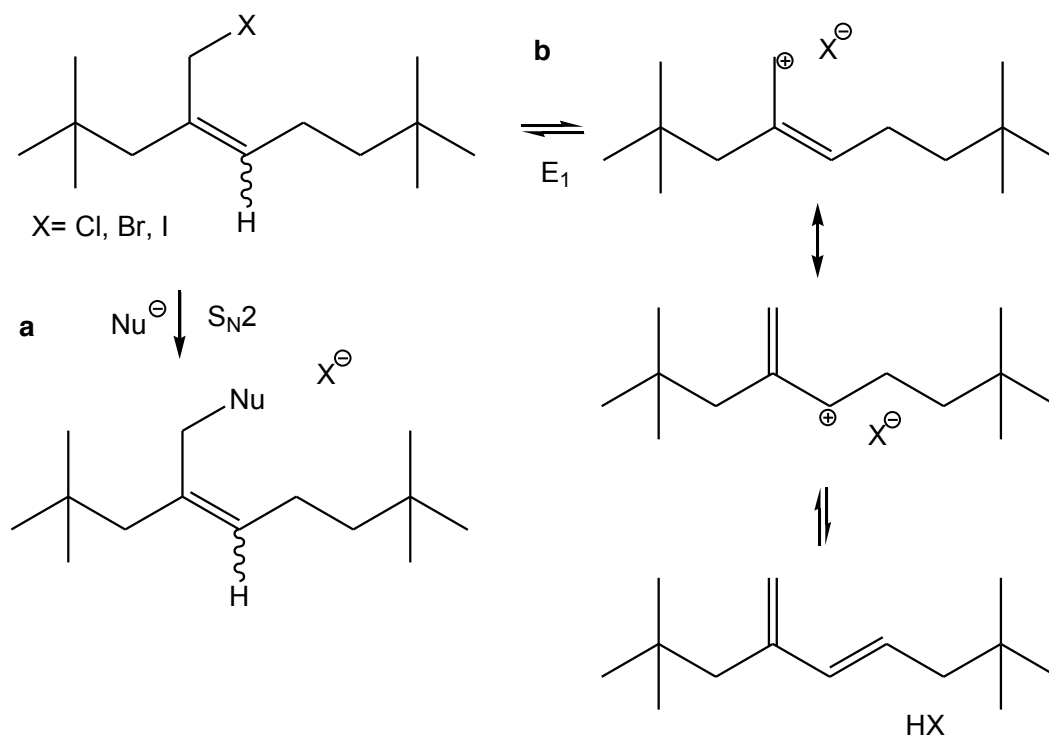
Chapter 3. Halobutyl Rubbers: Thermal Stability and Reactivity Towards Nucleophilic Substitution

3.1 Introduction

Halogenated butyl rubber contains allylic halide functionality which increases its reactivity towards a wide range of nucleophiles and provides a foundation for further derivatization of butyl rubber. The most important commercial process for producing butyl rubber derivatives is the vulcanization of BIIR through sulfuration to produce a cross-linked derivative of butyl rubber¹. A selection of butyl rubber derivatives have also been produced through reactions of BIIR with nitrogen,^{2,3} oxygen⁴ and phosphorus⁵ nucleophiles.

Previous observations have concluded that (*E,Z*)-*endo*-bromomethyl functionality in the presence of a nucleophile is likely to react through an S_N2 mechanism (Scheme 3.1, pathway a). At increased temperatures, nucleophilic substitution occurs concurrently with dehydrohalogenation resulting in the formation of HX and conjugated dienes (Scheme 3.1, pathway b). Butyl rubber derivatives, including r-CIIR, r-BIIR and r-IIIR, have been prepared through previous experimentation. The objective of the present study is to investigate the effect of the leaving group ability on the reactivity of these halogenated polymers with respect to thermal stability and nucleophilic substitution.

Scheme 3.1: Competing reaction pathways for halomethyl derivatives of butyl rubber (a. nucleophilic substitution; b. dehydrohalogenation)



3.2 Experimental

3.2.1 Materials

The following chemicals were used as received: Bromobutyl 2030 (LANXESS Inc $M_n \approx 400\,000$, allylic bromide content ≈ 0.15 mmol/g.), Chlorobutyl 1240 (LANXESS Inc, allylic chloride content ≈ 0.21 mmol/g), tetrabutylammonium acetate (TBAC, 97%, Sigma-Aldrich), tetrabutylammonium bromide (TBAB, 99%, Sigma-Aldrich), tetrabutylammonium iodide (TBAI, 98%, Sigma-Aldrich), tetrabutylammonium chloride (TBAC), N-butylimidazole (NBuI) and sulfur (LANXESS Inc). Acetone (ACS, Fisher Scientific), toluene (ACS, Fisher Scientific), xylenes (ACS, Fisher Scientific), dodecane

(ACS, Fisher Scientific), chloroform-d (99.8 atom % D, Sigma-Aldrich). All reagent equivalencies were calculated on a molar basis with respect to the 0.15 mmol/g of allylic bromide found in BIIR. All reactions were performed in a round bottom flask equipped with a Teflon® magnetic stir bar and under reflux, unless otherwise specified.

3.2.2 Thermal Stability Reactions

A solution of a halomethyl derivative of butyl rubber (r-CIIR, r-BIIR, r-IIIR) (2 g) in toluene (65°C and 100°C), xylenes (135°C) or dodecane (190°C) with Proton Sponge® (1.5 eq., 0.09 g, 0.450 mmol) was heated for varying amounts of time (5-20 h) at various temperatures (65°C, 100°C, 135°C or 190°C) depending on the material. The product was recovered by precipitation from acetone and dried under vacuum at room temperature. Samples withdrawn at regular intervals were characterized by ¹H NMR (in CDCl₃) spectroscopy with integration to an accuracy of ± 5%: For allylic chlorides, δ 5.01 (Exo-Cl, =CHH, 1H, s); δ 4.11 (Z/E-Cl-Me, =C-CH₂-Cl, 2H, s); for allylic bromides, δ 5.01 (Exo-Br, =CHH, 1H, s); δ 4.11 (E-BrMe, =C-CH₂-Br, 2H, s), δ 4.09 (Z-BrMe, =C-CH₂-Br, 2H, s); for allylic iodide, δ 4.08 (E-I-Me, =C-CH₂-I, 2H, s); δ 3.99 (Z-I-Me, =C-CH₂-I, 2H, s); for exo-conjugated diene butyl rubber, 6.05 (-CH=C(CH₃)-CH=, 1H, d); for endo-conjugated diene butyl rubber, 5.93 (=C(CH₃)-CH=, 1H, d). This procedure has been adapted from previous work.⁶

3.2.3 Alkylation of N-butylimidazole

A solution of halomethyl derivatives of butyl rubber (r-CIIR, r-BIIR, r-IIIR) (4 g) in toluene (100°C) or xylenes (135°C) with N-butylimidazole (6 eq., 0.447 g, 3.8 mmol) was

heated for varying amounts of time (5-20 h) at various temperatures (100°C or 135°C) depending on the material. The product was recovered by precipitation from acetone and dried under vacuum at room temperature. Samples withdrawn at regular intervals were characterized by ^1H NMR (in CDCl_3) spectroscopy with integration to an accuracy of $\pm 5\%$: For allylic chlorides, δ 5.01 (Exo-Cl, = CHH , 1H, s); δ 4.11 (Z/E-Cl-Me, = $\text{C-CH}_2\text{-Cl}$, 2H, s); for allylic bromides, δ 5.01 (Exo-Br, = CHH , 1H, s); δ 4.11 (E-BrMe, = $\text{C-CH}_2\text{-Br}$, 2H, s); δ 4.09 (Z-BrMe, = $\text{C-CH}_2\text{-Br}$, 2H, s); for allylic N-butylimidazole, δ 4.43 (N- $\text{CH}_2\text{-(CH}_2\text{)}_2\text{-CH}_3$, 2H, t); for exo-conjugated diene butyl rubber, 6.05 (- $\text{CH=C(CH}_3\text{)-CH=}$, 1H, d); for endo-conjugated diene butyl rubber, 5.93 (=C(CH₃)- CH= , 1H, d). This procedure has been adapted from previous work.³

3.2.4 Tetrabutylammonium Acetate Esterification

A solution of halomethyl derivative of butyl rubber (r-CIIR, r-BIIR, r-IIIR) (2 g) in toluene was heated to 65°C or 100°C for 60 min with tetrabutylammonium acetate (1 eq., 0.090 g, 0.3 mmol) The product was recovered by precipitation from acetone and dried under vacuum at room temperature. Samples withdrawn at regular intervals were characterized by ^1H NMR (in CDCl_3) spectroscopy with integration to an accuracy of $\pm 5\%$: For allylic chlorides, δ 5.01 (Exo-Cl, = CHH , 1H, s); δ 4.11 (Z/E-Cl-Me, = $\text{C-CH}_2\text{-Cl}$, 2H, s); for allylic bromides, δ 5.01 (Exo-Br, = CHH , 1H, s); δ 4.11 (E-BrMe, = $\text{C-CH}_2\text{-Br}$, 2H, s); δ 4.09 (Z-BrMe, = $\text{C-CH}_2\text{-Br}$, 2H, s); for allylic acetate, δ 4.43 (Z-OAc, = $\text{CH}_2\text{-O-CO-CH}_3$, 2H, s), δ 4.51 (E-OAc, = $\text{C-CH}_2\text{-O-CO-CH}_3$, 2H, s); for exo-conjugated diene

butyl rubber, 6.05 (-CH=C(CH₃)-CH=, 1H, d); for endo-conjugated diene butyl rubber, 5.93 (=C(CH₃)-CH=, 1H, d). This procedure has been adapted from previous work.⁴

3.2.5 Vulcanization of Halobutyl Rubbers with Sulfur

Dried r-CIIR, r-BIIR, r-IIIR (5.0 g) and solution treated BIIR and CIIR (5.0 g) were mixed with sulfur (1.5 phr, 0.075 g), using a two-roll mill (approximately 15 runs through to achieve full mixing). A 5.0 g sample of the uncured material was charged to an Advanced Polymer analyzer (Alpha Technologies, Canada) operating with 3 degrees of arc at a frequency of 1 Hz at various temperatures (65°C, 135°C, 160°C and 190°C) for 60 min. This procedure has been adapted from previous work.¹

3.2.6 Instrumentation and Analysis

¹H-NMR spectra were acquired in CDCl₃ (1H 7.26 ppm) at 400 MHz on a Bruker Avance-400 spectrometer, at 500 MHz on a Bruker Avance-500 spectrometer or at 600 MHz on a Bruker Avance-600 spectrometer. All chemical shifts were referenced to deuterated chloroform (CDCl₃). Rheological characterization was carried out in an oscillatory rheometer (Advanced Polymer Analyzer 2000, Alpha Technologies, Canada) operating in a parallel plate configuration.

3.3 Results and Discussion

3.3.1 Thermal Stability of Halobutyl Rubbers

The dynamics of the dehydrohalogenation of halomethyl derivatives of butyl rubber, including r-CIIR, r-BIIR, r-IIIR, were investigated and the results are summarized in Figure 3.1. Throughout this work, concentrations of conjugated dienes are listed as mmoles of functionality per gram of elastomer (mmol/g XIIR), while Proton Sponge® concentrations are expressed as molar equivalents relative to the mmol/g of allylic halide present in the starting material. It should be noted that each material has an initial concentration of conjugated dienes (0-10%) due to previous elimination reactions during the polymer preparation however the recorded concentration of conjugated dienes is representative of the dehydrohalogenation that occurs during the present reaction only.

Initially, the materials were reacted in a 10 wt% XIIR toluene solution at 100°C with 1.5 equivalents Proton Sponge® to form a basis for comparison. The reaction rate at 100°C increased in the following order: r-CIIR < r-BIIR < r-IIIR. As expected, the order of reactivity correlates directly with leaving group ability. Iodide is the best leaving group because bond dissociation energy is the lowest compared to bromide and chloride; therefore it is the most stable anion. Since iodide is the most favourable leaving group, the allyl iodide functionality is more prone to ionization (Scheme 3.1 b) than its chloride and bromide counterparts and, therefore, undergoes dehydrohalogenation to the highest conversion. Insight into the dehydrohalogenation characteristics of each polymer was achieved through reaction at various temperatures.

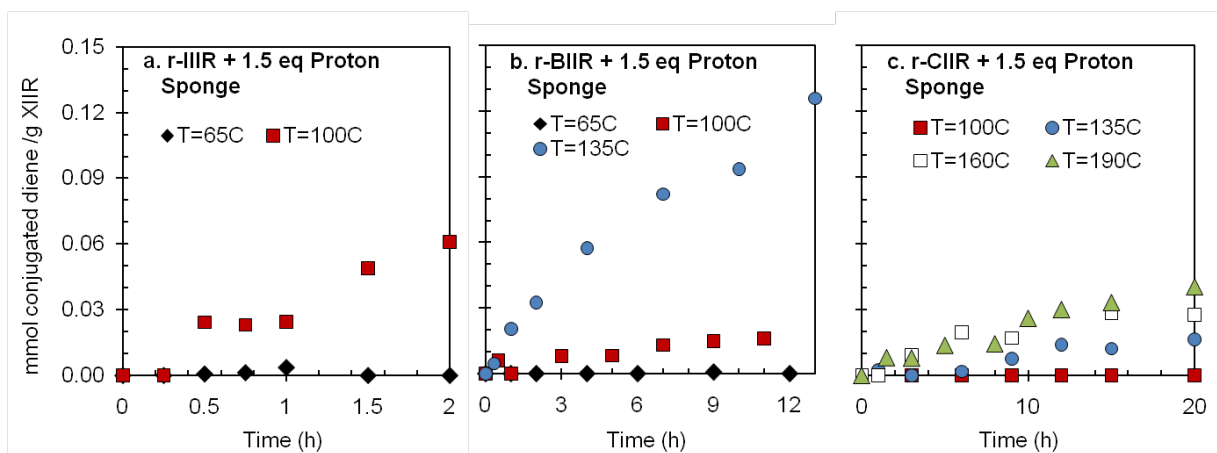


Figure 3.1: Conjugated diene evolution during dehydrohalogenation of butyl rubber derivatives (a. r-IIIR; b. r-BIIR; c. r-CIIR) at various temperatures (65°C in toluene, 100°C in toluene, 135°C in xylenes, 190°C in dodecane) with 1.5 eq Proton Sponge

The results of heating a 10 wt% toluene solution of r-IIIR to 65°C with 1.5 equivalents Proton Sponge[®] are summarized in Figure 3.1a. The reaction did not produce a notable concentration of conjugated dienes in the allotted time (2 h), indicating r-IIIR was stable to dehydrohalogenation at 65°C. Comparing these results to those of reaction at 100°C clearly indicate that r-IIIR is much less stable towards dehydrohalogenation at increased temperatures. The reaction at 65°C produced no conjugated dienes, while the reaction at 100°C produced a yield of 40% conjugated dienes. The lack of stability of r-IIIR towards dehydrohalogenation at 100°C makes it an unsuitable material for applications that contain high processing temperatures; however, it is a promising material for low temperature reactions.

The dehydrohalogenation reactions of 10 wt% r-BIIR solutions were studied at 65°C in toluene and 135°C in xylenes, respectively, with 1.5 equivalents Proton Sponge[®] and the results are summarized in Figure 3.1b. At 65°C, r-BIIR showed stability towards dehydrohalogenation; however, at increased temperatures the presence of conjugated dienes is noteworthy. The yield of conjugated dienes at 100°C was found to be 13% in the allotted time (11 h) and the rate of dehydrohalogenation increased significantly at 135°C, producing a yield of 90% conjugated dienes in the reaction time (13 h). The polymer containing allylic bromomethyl functionality was unstable towards dehydrohalogenation at 135°C; however, its thermal stability at 100°C makes it ideal for applications which process at approximately this temperature.

The dehydrohalogenation dynamics of 10 wt% r-CIIR solutions were investigated at 135°C (in xylenes), 160°C (in dodecane) and 190°C (in dodecane), respectively, with 1.5 equivalents of Proton Sponge[®]. The results were compared to the reaction completed at 100°C (in toluene) and are summarized in Figure 3.1c. It was determined that r-CIIR was thermally stable at 100°C and 135°C and a small amount of dehydrohalogenation in the allotted time (20 h). A decreased stability of r-CIIR with respect to dehydrohalogenation at reaction temperatures of 160°C and 190°C is noted, with yields of 18% and 27% conjugated dienes, respectively, in the allotted time (20 h). The excellent thermal stability of r-CIIR allows it to be processed at higher temperatures than the bromide derivative, making it an exceptional for processing at higher temperatures.

3.3.2 N-Alkylation of N-butylimidazole with Halobutyl Rubbers

As stated earlier, N-butylimidazole (BuIm) has been investigated as a potential nucleophile for N-alkylation of BIIR (Chapter 1, Scheme 1.11). The resulting elastomeric ionomer has a versatile imidazole ring that provides a foundation for investigating derivatives of BIIR with various pendant functional groups. For this reason, the reactivity of each halobutyl rubbers towards BuIm was studied.

The dynamics of the N-butylimidazole (BuIm) alkylations of halomethyl derivatives of butyl rubber, which include r-CIIR, r-BIIR and r-IIIR, were analyzed and the results are summarized in Figure 3.2. The temperatures of the reactions were tailored to the specific halobutyl rubber and were based on previous thermal stability studies. Throughout this work, concentrations of imidazolium halide and conjugated dienes are listed as mmoles of functionality per gram of elastomer (mmol/g XIIR), while BuIm concentrations are expressed as molar equivalents relative to the mmol/g of allylic halide present in the starting material. Initial conjugated diene concentrations (0-10%) present in the starting material as a results of previous isomerization reactions, are not included in the recorded concentration of conjugated dienes, similar to the thermal stability study. Similarly to the reactants utilized for analysis of thermal stability, the initial concentration of conjugated dienes (0-10%) present in the starting material as a result of the previous isomerization reactions during the polymer preparation are not included in the recorded concentration of conjugated dienes.

Figure 3.2a and 3.2d summarizes the reactions of 10 wt% r-IIIR in toluene solutions with 6 molar equivalents BuIm at 65°C and 100°C, respectively. At both temperatures, r-IIIR

undergoes an S_N2 reaction to successfully produce BuIm N-alkylation products. At 65°C, the reaction proceeds slowly, forming a 75% ionomer yield in the allotted time (10 h) with additional allylic iodide functionality available for further reaction. The concentration of conjugated dienes is also minimal at this reaction temperature, consistent with previous thermal stability studies. A notable concentration of conjugated dienes was produced when the reaction temperature was increased to 100°C, indicating there is competition between S_N2 and E1 pathways (Scheme 3.1). All the allylic iodide functionality was consumed in the allotted time (9.5 h), producing a 70% yield of alkylation products, while the remaining 30% was conjugated dienes.

The BuIm alkylation reactions of 10 wt% r-BIIR solutions were studied at 100°C (in toluene) and 135°C (in xylenes) with 6 molar equivalents BuIm and the results are summarized in Figure 3.2b and 3.2e, respectively. At both 100°C and 135°C, r-BIIR achieved a final ionomer yield of approximately 90%, while the remaining 10% was attributed to conjugated dienes formation. As expected, the rate of ionomer formation was faster at 135°C than 100°C due to the temperature dependency of S_N2 reactions. Although r-BIIR was shown to be thermally unstable at 135°C, introduction of BuIm to the system caused nucleophilic substitution to become the dominant pathway (Scheme 3.1, pathway a) over dehydrohalogenation.

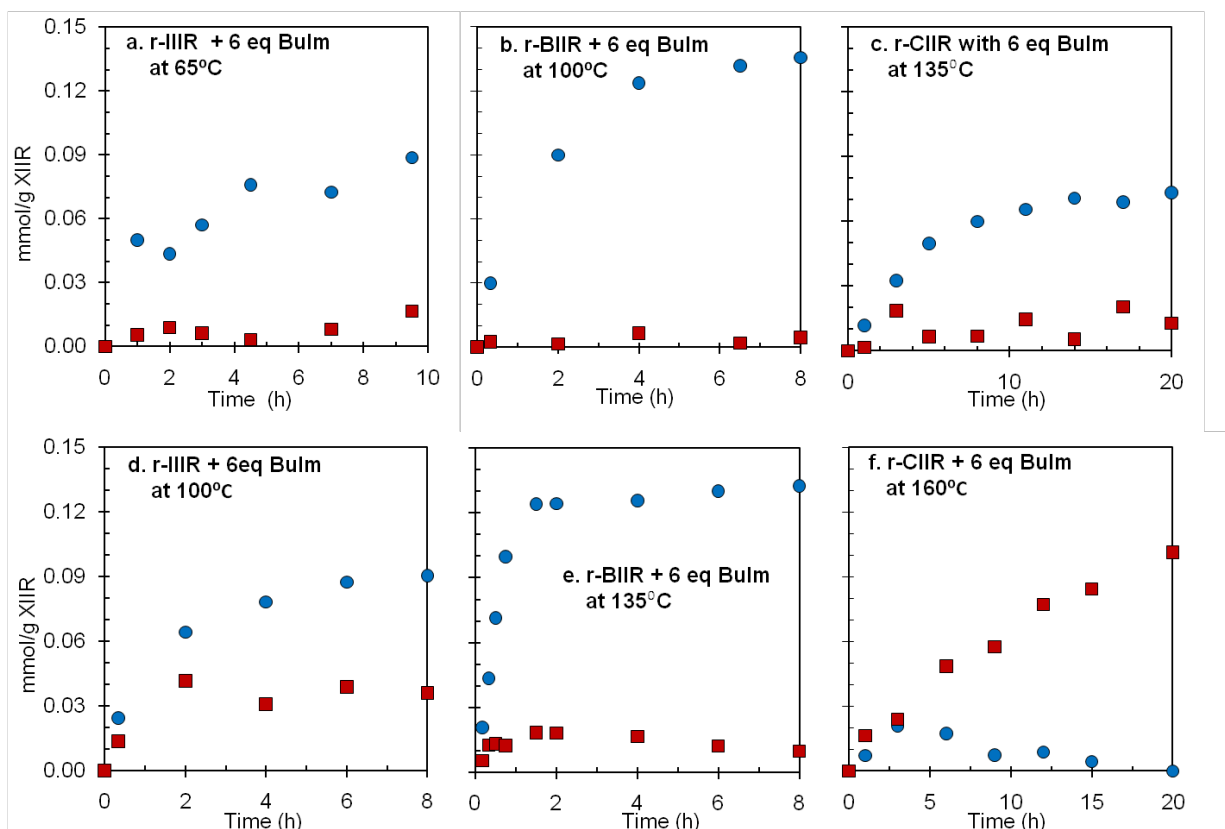
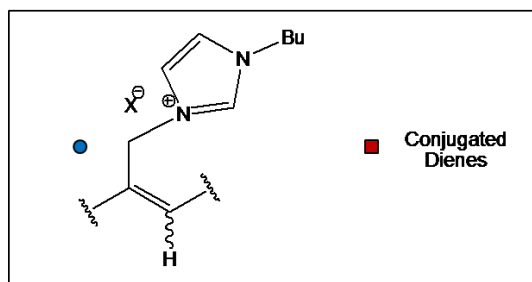


Figure 3.2: Dynamics of BuIm alkylations in solutions of 10 wt% halobutyl rubber derivatives (a/d. r-IIIR; b/e. r-BIIR; c/f. r-CIIR) at various temperatures (65°C in toluene, 100°C in toluene, 135°C in xylenes, 190°C in dodecane) with 6 eq N-butylimidazole

Figure 3.2c and 3.2f summarizes the reactions of 10 wt% r-CIIR solutions with 6 molar equivalents BuIm at 135°C (in xylenes) and 160°C (in dodecane), respectively. At 135°C, the reaction proceeded to a steady state with a final imidazolium chloride:allylic chloride:conjugated dienes ratio of 50:40:10. Since S_N2 reaction kinetics are sensitive to

nucleophile concentration, a higher loading of BuIm would push the reaction towards complete conversion; however, in order to compare the reaction dynamics of the three materials equally, the experimental conditions were kept constant. When the temperature of reaction was set to 160°C, competition between S_N2 and E1 pathways (Scheme 3.1) was observed as both alkylation products and conjugated dienes were produced concurrently for the first 3 hours. After 3 hours, dehydrohalogenation continued at a rapid pace and the alkylation products were consumed. Since BuIm is a base as well as a nucleophile, it is likely that deprotonation by BuIm becomes more favoured than nucleophilic substitution with an increase in temperature from 135°C to 160°C. Ionomer formation occurs at low conversion at 135°C, but at 160°C, a change in BuIm reactivity results in rapid dehydrohalogenation.

It is understood from the results summarized in Figure 3.2 that the leaving group ability of the displaced halide correlates directly with the reaction dynamics for N-alkylations of BuIm with halobutyl rubbers. Since iodide is the most favourable leaving group, r-IIIR has the unique ability to undergo nucleophilic substitution with BuIm at low temperatures. The disadvantage associated with r-IIIR is its susceptibility toward dehydrohalogenation at high temperatures. Since the nucleophilic substitution reaction pathway competes with the dehydrohalogenation pathway, r-IIIR is only practical in a limited temperature range. The temperatures utilized in this study for the BuIm alkylation with r-BIIR were ideal for producing alkylation products with little byproducts. At higher temperatures, it is likely that dehydrohalogenation (Scheme 3.1, pathway b) would

dominate observed products of the reaction. The reaction rate for r-CIIR with BuIm at 135°C was significantly slower than those for r-BIIR under the same conditions. These results are expected, as chloride is a less favourable leaving group than bromide.

3.3.3 Tetra-*n*-butylammonium Acetate Esterification of Halobutyl Rubbers

The reactivity of BIIR with carboxylate nucleophiles, such as quaternary ammonium carboxylate salts (TBAAc) (Chapter 1, Scheme 1.8) has been of interest to prepare butyl rubber derivatives containing pendant polymerizable functionality. Consequently the reactivity of each halobutyl rubber towards TBAAc was studied.

Figure 3.3 summarizes the dynamics of the esterification of halomethyl derivatives of butyl rubber, including, r-CIIR, r-BIIR, r-IIIR, with tetra-*n*-butylammonium acetate (TBAAc). The polymers were reacted in a 10 wt% XIIR toluene solution at either 65°C or 100°C with 1 molar equivalent TBAAc. Throughout this work, concentrations of allylic ester functionality and conjugated dienes are listed as mmoles of functionality per gram of elastomer (mmol/g XIIR), while TBAAc concentrations are expressed as molar equivalents relative to the mmol/g of allylic halide present in the starting material. In keeping with the previous reactions, initial concentrations of conjugated dienes (0-10%) due to previous isomerization reactions during polymer preparation are not included in the recorded conjugated dienes concentration.

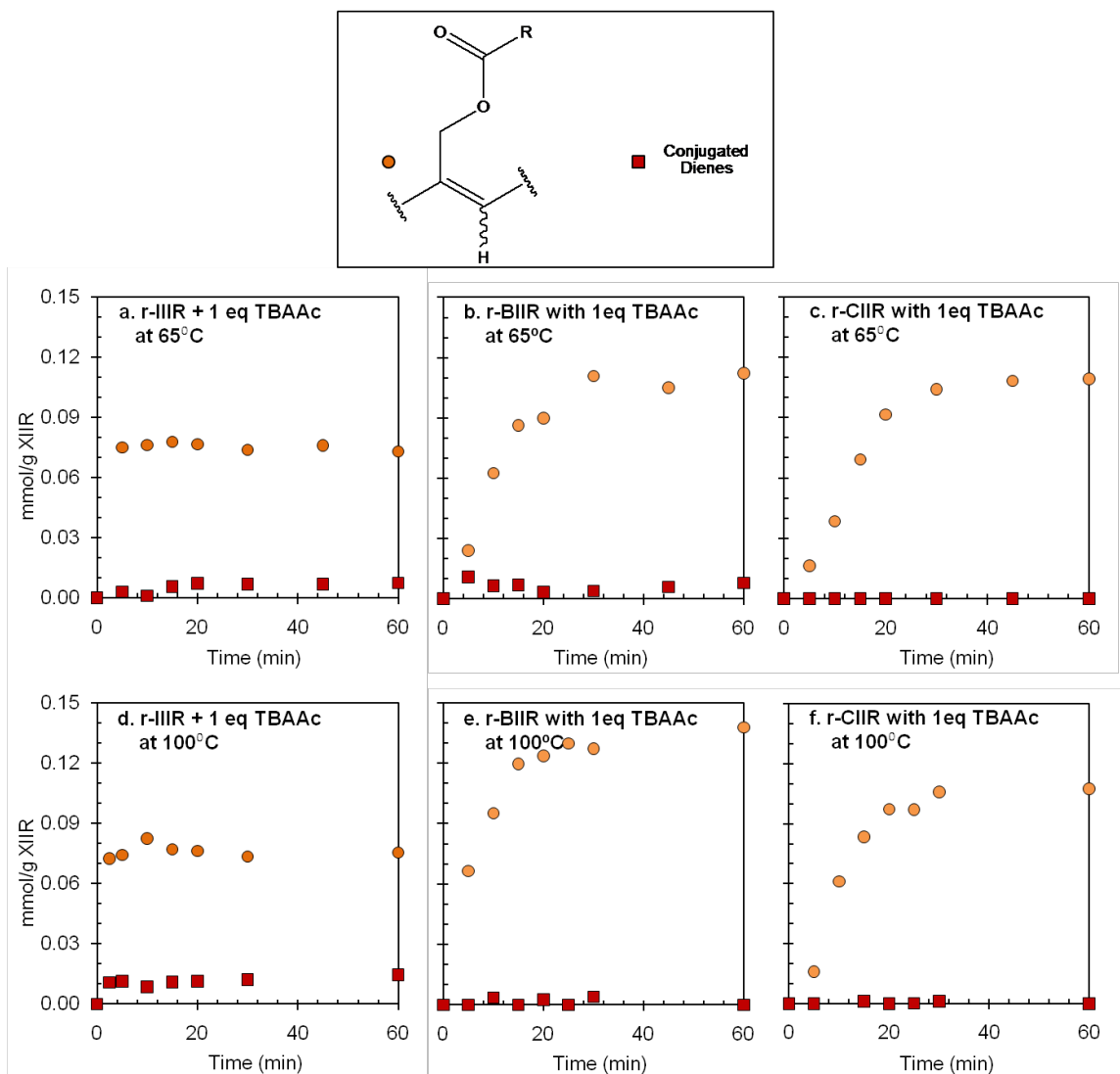


Figure 3.3: Esterification dynamics for halobutyl rubber derivatives (a./d. r-IIIR; b./e. r-BIIR; c./f. r-CIIR) at various temperatures (65°C and 100°C in toluene) with 1 eq TBAAc

Figure 3.2a and 3.2d summarize the reaction of r-IIIR with TBAAc at both 65°C and 100°C, respectively. At both temperatures, a 70% yield of allylic ester product was achieved in the first 5 minutes of the reaction. An increase in dehydrohalogenation was observed when the temperature was increased from 65°C to 100°C, as expected. Reaction of r-BIIR with TBAAc at 65°C (Figure 3.3b) and 100°C (Figure 3.3e) achieved a 90%

yield of allylic ester products in 1 hour, for both reactions. The polymer was generally unreactive towards dehydrohalogenation and as a result minimal concentrations of conjugated dienes were observed. Similarly, the polymer containing (*E,Z*)-*endo*-chloromethyl functionality was reacted with TBAAc at 65°C (Figure 3.3c) and 100°C (Figure 3.3f). At both temperatures, a 75% yield of allylic ester products was achieved in the allotted time (1 h). As expected, dehydrohalogenation was not observed at these low temperatures.

An increase in reactivity was noted for each polymer when the reacting nucleophile was changed from BuIm to TBAAc. This observation was expected since TBAAc is more nucleophilic than BuIm. The polymer containing (*E,Z*)-*endo*-iodomethyl functionality showed the fastest reactivity toward nucleophilic substitution with TBAAc, reaching high conversion in the first 5 minutes of the reaction. This follows the trend of leaving group ability, as iodide is the best leaving group however the similar reactivity of *r*-CIIR and *r*-BIIR towards TBAAc provided an exception to the expected reactivity trend based on leaving group ability. The leaving group ability of the halide is dependent on the stability of the resulting halide anion and bond dissociation energy of the carbon-halide bond. Since the tetrabutylammonium ion is not a passive counter-ion, it is likely to actively assist in the removal of the departing halide ion by stabilizing it through hydrogen bonding and electrostatic interactions. This would reduce the significance of the reactivity on the leaving group ability.

3.3.4 Vulcanization of Halobutyl Rubbers with Sulfur

An investigation of the effect of leaving group ability on the solid-state sulfuration of halobutyl rubbers at 160°C was completed and the results are summarized in Figure 3.4. A temperature of 160°C was studied as it is a standard vulcanization temperature used in industry. The polymer containing (*E,Z*)-*endo*-iodomethyl functionality showed no reactivity towards sulfur at this curing temperature. This observation is most likely a result of the poor thermal stability of r-IIIR with rapid and complete formation of conjugated dienes, which are much less reactive towards sulphur than the allylic halide functionality. Both r-CIIR and r-BIIR successfully produced cross-linked networks, as evidenced by the increase in storage modulus; however, r-CIIR cured to a greater extent than its bromide counterpart. At these temperatures, r-BIIR experienced significant dehydrohalogenation, which decreased the reactivity of the material towards sulphur.

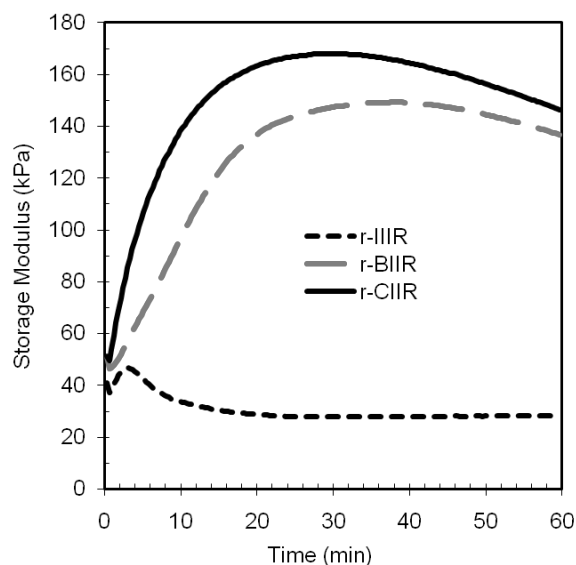


Figure 3.4: Vulcanization of halobutyl rubbers (r-IIIR, r-BIIR, r-CIIR) with sulphur (1.5 phr) at 160°C

Insight into the effects of microstructure on the reactivity of halobutyl rubbers with sulphur were examined by studying the dynamics of exomethylene halide and halomethyl derivatives of chlorobutyl rubber and bromobutyl rubber. Both the Exo-Cl and Exo-Br materials were solution treated to remove epoxide and other stabilizers to ensure all materials were consistently compared. Each material was cured at 160°C using 1.5 phr sulfur and the results are summarized in Figure 3.5.

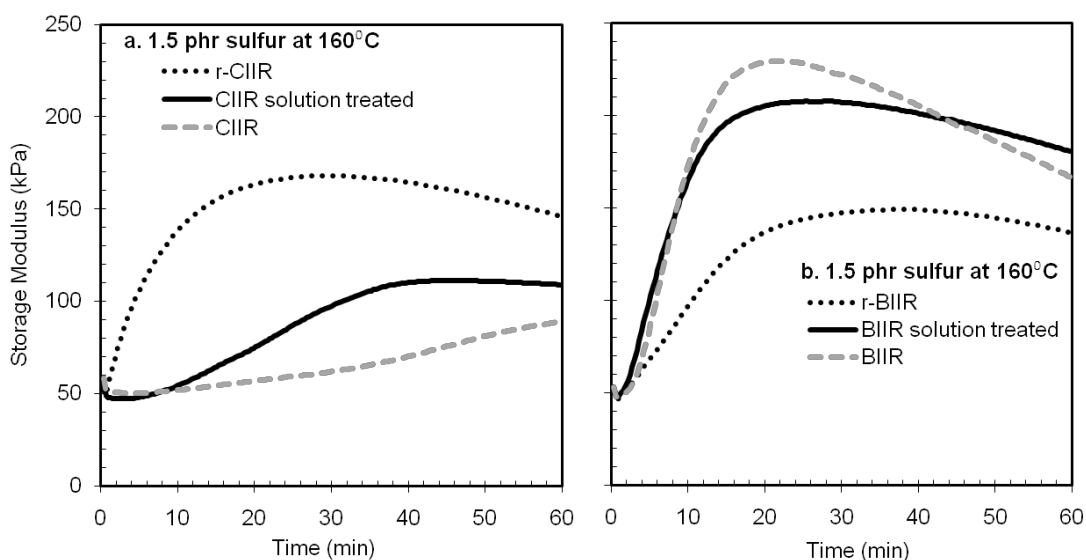


Figure 3.5: Vulcanization of butyl rubber derivatives (a. r-CIIR, solution-treated CIIR, CIIR; b. r-BIIR, solution treated BIIR, BIIR) with sulphur (1.5 phr) at 160°C

When Exo-Cl and (*E,Z*)-*endo*-chloromethyl isomers were sulfur cured (Figure 3.5a), it became evident that (*E,Z*)-*endo*-chloromethyl functionality had a higher affinity for sulfur than the Exo-Cl functionality due to the formation of a more cross-linked network (as shown by the increase in storage modulus) in the allotted time (1 h). Hopkins et al.

also observed a lack of reactivity of commercial CIIR toward sulfur.⁷ Previous analysis (Section 2.3.2) proved that Exo-Cl had limited reactivity, since it was not susceptible to S_N2' isomerization. Altering the microstructure from Exo-Cl functionality to (*E,Z*)-*endo*-chloromethyl functionality benefited the cure as it made the polymer more reactive to sulphur.

The different bromide isomers (Figure 3.5b) were observed to have the opposite reactivity toward sulphur in comparison to the chloride isomers. The Exo-Br functionality formed a material with a higher storage modulus than the (*E,Z*)-*endo*-bromomethyl functionality. Although isomerization of Exo-Br to (*E,Z*)-*endo*-bromomethyl functionality increases its reactivity, the Exo-Br isomer is less susceptible to dehydrohalogenation than the *r*-BIIR isomers (Appendix A2). This is an important consideration since the reaction temperature is high enough to promote dehydrohalogenation.

3.4 Conclusions

Halomethyl (*r*-CIIR, *r*-BIIR and *r*-IIR) isomers were prepared from BIIR and the effect of leaving group on thermal stability and reactivity towards various nucleophiles was compared. *r*-CIIR displayed the greatest thermal stability, while *r*-IIR polymer readily underwent dehydrohalogenation at temperatures above 65°C. The instability of *r*-IIR towards dehydrohalogenation at high temperatures makes it an unsuitable material for applications that require high processing temperatures; however, it is a promising

polymer for low temperature reactions. The thermal stability of r-CIIR surpasses its bromide counterpart and presents a new temperature range for processing butyl rubber derivatives.

The reactivity of halobutyl rubbers were compared by reacting each polymer with three different nucleophiles; BuIm, TBAAc and sulphur. Since iodide is the most favourable leaving group, r-IIIR had the unique ability to undergo nucleophilic substitution at low temperatures however competition between the nucleophilic substitution reaction pathway and dehydrohalogenation pathway at high temperatures limit the useful temperature range of r-IIIR. Bromide falls between chloride and iodide in leaving group ability, allowing r-BIIR to have the greatest balance between nucleophilic substitution and dehydrohalogenation. Since chloride was the least favourable leaving group, r-CIIR had the greatest thermal stability however it was less susceptible to nucleophilic substitution by BuIm than r-BIIR. The lack of reactivity of r-CIIR was not consistent with all nucleophiles, as reaction dynamics with TBAAc display its variable reactivity towards nucleophilic substitution with results parallel to those of r-BIIR. The r-CIIR polymer's resistance to dehydrohalogenation was demonstrated at high temperature sulphur cure, out-curing its bromide counterpart.

3.5 References

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Chapter 4. Conclusions and Future Work

The influence of leaving group and microstructure on the reactivity of r-CIIR, r-BIIR and r-IIIR were investigated. Halobutyl rubbers with comparable microstructures were prepared and characterized. The thermal stability and reactivity towards various nucleophiles were compared for each of the halobutyl rubber derivatives.

4.1 Microstructure and Model Compound

Brominated, chlorinated and iodinated derivatives of butyl rubber with (*E,Z*)-*endo*-halomethyl functionality were prepared and characterized with the assistance of model compounds. The isomerization of BIIR and CIIR were studied uncatalyzed, and in the presence of a Lewis acid catalyst and a nucleophilic catalyst. Both BIIR and CIIR readily isomerized when catalyzed with $\text{Zn}(\text{stearate})_2$, a Lewis acid, through allyl halide ionization, followed by recombination with rearrangement. BIIR isomerized through an $\text{S}_{\text{N}}2'$ mechanism when TBAB was employed, with bromide acting as a nucleophilic catalyst. Chlorides inability of reacting through a $\text{S}_{\text{N}}2'$ mechanism was demonstrated by TBAC's unreactivity with respect to CIIR isomerization. When TBAC was reacted with BIIR, it resulted in both Exo-Cl and (*E,Z*)-*endo*-chloromethyl isomers, giving further evidence of TBACs inability to react through an $\text{S}_{\text{N}}2'$ mechanism with halogenated butyl rubbers. An excess of TBAI was shown to undergo halide exchange with both BIIR and r-BIIR to produce mainly (*E,Z*)-*endo*-iodomethyl, while the remaining product was composed of (*E,Z*)-*endo*-bromomethyl isomers.

4.2 Thermal Stability and Reactivity

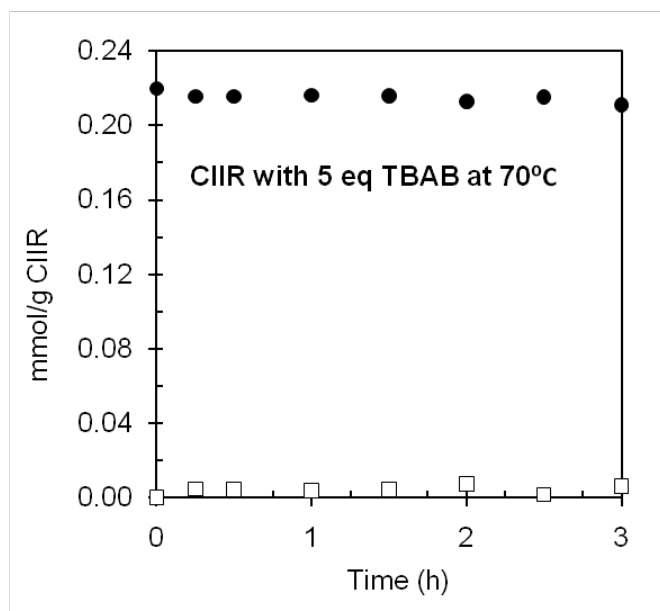
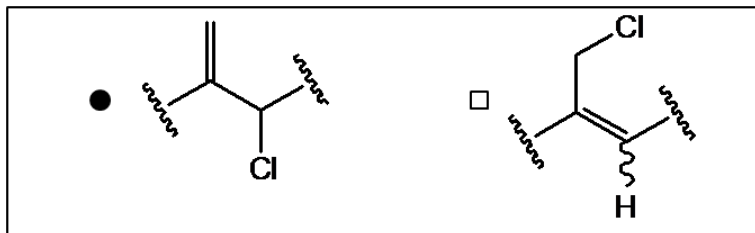
Halomethyl (r-CIIR, r-BIIR, r-IIIR) isomers were prepared from BIIR and the effect of leaving group on thermal stability and reactivity towards nucleophilic substitution were compared. The polymer containing (*E,Z*)-*endo*-iodomethyl isomers readily underwent dehydrohalogenation at temperatures above 65°C; however, it was reactive towards nucleophilic substitutions at low temperatures. The best balance between nucleophilic substitution reactivity and dehydrohalogenation was observed with the bromomethyl derivative (r-BIIR). Exceptional thermal stability at temperatures up to 190°C was displayed by the chloromethyl derivative (r-CIIR); however, it was at the expense of reactivity towards certain nucleophiles at lower temperatures. This lack of reactivity shown by r-CIIR was not consistent with all nucleophiles, as reaction dynamics with TBAAc display its variable reactivity towards nucleophilic substitution with results parallel to those of r-BIIR

4.3 Future Work

Further exploration into the factors which influence the equilibrium of Exo-X and (*E,Z*)-*endo*-halomethyl isomers during the isomerization of BIIR and CIIR is required to understand why full isomerization is not possible. Possible factors influencing this equilibrium could include reaction temperature and concentration of rubber in solution. The presence and type of catalyst used to assist in isomerization could also affect this equilibrium.

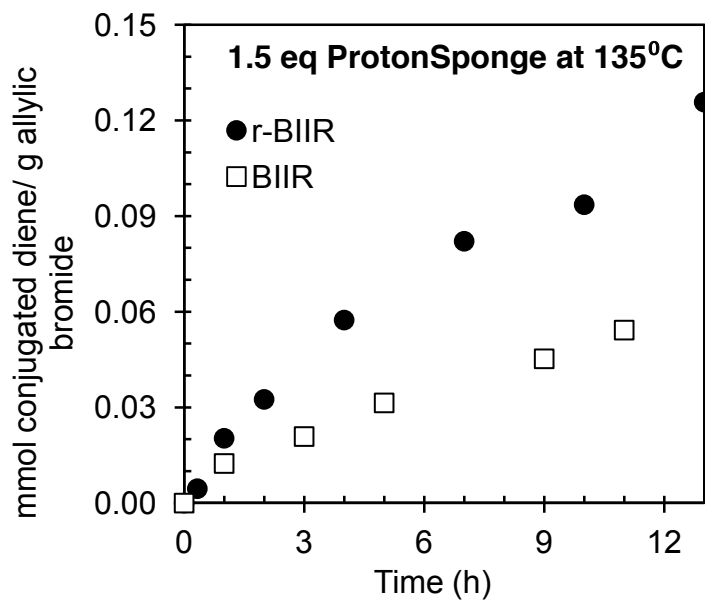
As r-CIIR has been observed to be suitable for high temperature processing, a practical method for preparing this material should be investigated. Also, further comparison of the halobutyl rubbers reactivity with different nucleophiles should be studied to gain insight into r-CIIRs inconsistent reactivity toward nucleophilic substitutions.

Appendix A1: CIIR Isomerization with TBAB



The reaction dynamics of a 10 wt% solution of CIIR in THF with 5 eq TBAB at 70°C to further investigate the reactivity of CIIR toward isomerization or halide exchange.

Appendix A2: Dehydrohalogenation of BIIR and r-BIIR



Evolution of conjugated dienes due to dehydrohalogenation of brominated butyl rubber (BIIR) and isomerized brominated butyl rubber (r-BIIR) at 135°C with 1.5 eq Proton Sponge®.