Nucleophilic Catalysis of Brominated Butyl Rubber Substitution Reactions

By

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Abstract

The allylic bromide functionality within brominated poly(isobutylene-co-isoprene), or BIIR, is amenable to substitution by a wide range of nucleophiles. The objective of this work was to gain insight into the dynamics of these substitution reactions, and to develop methods for accelerating these processes. Of particular interest was the reactivity of exomethylene (Exo-Br) and bromomethyl (BrMe) isomers found within BIIR toward various nucleophiles, and catalytic techniques for affecting the proportion of these isomers.

BIIR isomerization can be catalyzed through ionic chemistry involving soluble Lewis acids such as zinc stearate and through a nucleophilic $S_N 2$ ' rearrangement with soluble bromide salts such as tetrabuylammonium bromide (TBAB). The compatibility of TBAB with other nucleophiles makes it a preferable choice, but further rate enhancements can be realized using the corresponding iodide salt (TBAI). TBAI serves not only as nucleophilic isomerization catalyst, but also accelerates halide displacement from BIIR by an *in-situ* formation of an allylic iodide intermediate.

Studies of BIIR isomerization and substitution reactions involved solvent-borne reactions of tetrabutylammonium acetate (TBAAc) and solvent-free reactions with PPh₃ and 2-[2- (dimethylaminoethoxy)ethanol]. In all cases, the BrMe isomers were more reactive to nucleophilic substitution than Exo-Br. Since the esterification of BIIR with TBAAc generates TBAB as a reaction by-product, displaced bromide catalyzes the isomerization of Exo-Br to the more reactive BrMe isomers. As a result, these esterifications exhibit auto-accelerating

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dynamics. Similar behaviour is observed for solvent-fee alkylations of PPh_3 and tertiary amines, since the resulting onium bromide salts are effective isomerization catalysts. All reactions show some increase in rate with the addition of TBAI, supporting the concept of nucleophilic catalysis.

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Chapter 1. Introduction

1.1 Poly(isobutylene-co-isoprene) Rubber

Butyl rubber (IIR) is an elastomeric copolymer of isobutylene with 1-2% isoprene that is produced on a kilotonne scale as a raw material for tire inner liner applications. This market use exploits the exceptional gas impermeability and oxidative stability of IIR. However, vulcanization is required to transform IIR into thermoset rubber product with the mechanical strength and creep resistance demanded by tire manufacturers. With an unsaturation content far below that of the diene-rich elastomers used in tire treads and sidewalls, IIR does not cross-link as quickly when cured with standard sulfur-based formulations. Since all components of a tire are cured at the same temperature for the same amount of time, the reactivity of IIR is insufficient for the inner liner market.

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

1.2 Halogenation

Halogenation of IIR to introduce allylic halide functionality is one way of increasing the reactivity of butyl rubber toward sulfur and other nucleophiles. Currently, commercial forms of brominated and chlorinated butyl rubber are available, and a considerable volume of literature has focused on olefin halogenations in general, which has facilitated studies of IIR halogenation in particular.

Chlorination experiments conducted with trans-2-butene and isobutylene by Poutsma et al.¹ outlined the halogenation of alkenes through both radical and ionization pathways. Halogenation of trans-2-butene gave mainly the addition product, while reactions with isobutylene favoured the substitution product. The substitution product was indicative of halogenation through an ionization pathway, rather than a radical mechanism which favours the evolution of addition products with alkenes. Their work demonstrated that higher substituted alkenes favoured halogenation via an ionic pathway.





It is now widely accepted that bromination of alkenes occurs by electrophilic addition across the double bond. Halogenation of ethylene and the resulting isomer distribution of the products provided insight into the mechanism of reaction.² The predominance of one geometric isomer (cis vs. trans) over another after halogenation suggested that an intermediate structure existed that was inhibiting rotation of the carbon-carbon double bond. The formation of a halonium ion, or in the case of bromination, bromonium ion, explained the observed distribution of products.

Scheme 1.2 : Bromination of Ethylene



The stability of halonium ions was investigated with work by Brown et al..³ They used X-ray diffraction techniques to characterize the bromonium and iodonium triflate salts of adamantylideneadamantane (Ad = Ad). Isolation of these compounds lead to the calculation of bond lengths and bond angles. Their work allowed for the determination of rate constants for the exchange of the halonium ion between olefins. The process was found to be interaction dependent, relying only on entropy-driven collisions for transfer of the halogen from one olefin to another.

Determining product distributions in butyl rubber, and in polymers in general, is more difficult than for small molecules. However, the characterization of halogenation products within butyl rubber can be accomplished using a model compound that mirrors the structure of the polymer's reactive functionality. Whereas structural characterization of elastomeric products is complicated by extended relaxation times in NMR experiments and low olefin concentrations (1-2% isoprene), model compound mixtures can be fractionated and studied by high resolution NMR spectroscopy and mass spectrometry. Vukov studied 2,2,4,8,8-pentamethyl-4-nonene (PMN) reactions to characterize the reaction products of IIR bromination and chlorination.⁴

Vukov observed that halogenations of PMN and IIR yielded only the substitution product (Scheme 1.3). The exomethylene (**1a**) isomer is the kinetically favoured product and accounts for 90% of allylic bromide functionality in the rubber, whereas the remaining 10% is the more thermodynamically stable bromomethyl (**1b**) isomer. Vukov suggested that a lack of addition products is the result of steric interactions with the large quaternary groups that surround the carbon-carbon double bond. The bulkiness of the alkyl substituents prevented nucleophilic attack of free bromide ions on the bromonium ion resulting from electrophilic addition.





Industrial bromination of butyl rubber is conducted in hexanes solution to give the allylic substitution product, with HBr as a reaction by-product. Since one bromine atom is lost as HBr for every substitution, only a maximum of 50 wt% of bromine can be incorporated into the polymer. Increasing bromine efficiency is desirable both economically and environmentally as it would reduce HBr waste. For these reasons, research efforts have been directed towards preventing the formation of HBr during reaction, with the hopes of achieving bromine efficiencies greater than the current theoretical 50 wt%.

An Esso patent from 1958 outlines the use of peroxides in the bromination reaction. Introducing various amounts of a 30 wt% solution of hydrogen peroxide in water to bromination reactions, bromine efficiency was increased by as much as 70%.⁵ However, the use of peroxides to oxidize HBr back to Br₂ resulted in the incorporation of oxygen into the rubber, adversely affecting its stability. Ultimately, peroxides are too strong to use as oxidizers for increasing bromine efficiency and cannot be used without changing the microstructure of the rubber.

Bayer technology uses organic azo compounds and alkali metal/alkaline earth metal hypochlorites as more gentle reagents for HBr oxidation.⁶ A publication by Kaszas described the ability of sodium hypochlorite to oxidize HBr to molecular bromine, without introducing oxygen or chlorine into the rubber.⁷ Halogenations carried out at room temperature using 2 molar equivalents of NaOCl with respect to bromine resulted in bromine efficiency exceeding 50 wt%. However, this benefit was offset by lower halogenation rates, leading Kaszas to investigate the IIR halogenation further.⁸ Monitoring Br₂ concentrations revealed an initial period of rapid bromine consumption, which then slowed to a more moderate reaction velocity. He proposed a mechanism wherein bromine acted as a catalyst through electron donor/acceptor interaction with the bromonium ion intermediate, as shown in Scheme 1.4.

Scheme 1.4 : Bromine Catalyzed Halogenation



In this mechanism, bromine helps stabilize the bromonium ion transition state and lowers its activation energy, thus increasing the overall rate of bromination. The use of an electrophilic solvent in this system would help further stabilize the transition state intermediate and increase reaction rates. A 30/70 v/v mixture of methylene chloride and hexanes was used along with NaOCl to oxidize HBr back to bromine, resulting in 95 wt% bromine conversion in 1 minute.

1.3 Allylic Bromide Isomers in BIIR and Their Stability

Studies of BIIR and BPMN stability have provided insight into the performance of allylic bromide at vulcanization temperatures.⁹ Heating promotes the isomerization of Exo-Br to the thermodynamically more stable BrMe isomer. However, increased temperatures also result in dehydrobromination to give conjugated dienes (Scheme 1.5).

Scheme 1.5 : Stability of Allylic Bromide



Heating BPMN with a nearly 50:50 Exo-Br:BrMe starting isomer ratio to 145°C yielded an equilibrium distribution of 15:85 after 1 minute.⁹ The shift from Exo-Br to BrMe is accompanied by the formation of conjugated diene structures (2,3a,3b) from dehydrobromination. In BIIR, however, acid scavengers are present to sequester HBr and limit dehydrobromination, which not only leads to the formation of conjugated dienes, but can also reduce the molecular weight of the elastomer through β -scission of allyl cation intermediates.

1.4 Nucleophilic Substitution Reactions with BIIR

The reactivity of allylic halides has been investigated for a wide range of nucleophiles with the goal of producing new BIIR derivatives. Allylic halides generally undergo bimolecular nucleophilic substitution reactions ($S_N 2$) yielding substitution products at the α -carbon with loss of halide (Scheme 1.6). Reactions with allylic halides, however, also undergo abnormal $S_N 2$ reactions at the γ -carbon ($S_N 2$ ') with migration of the double bond.¹⁰

Scheme 1.6 : S_N2 Bimolecular Substitution



The substitution of the methyl group on the α -carbon in Scheme 1.6 with a larger *t*-butyl group imposes a steric hindrance on the approach of the nucleophile.¹¹ It is now easier for the nucleophile to attack at the γ -carbon of the carbon-carbon double bond.

Scheme 1.7 : S_N2' Abnormal Bimolecular Substitution



The above examples are analogous to the exomethylene isomer in BIIR (1a) where nucleophilic attack at the allylic bromide α -carbon is protected from large nucleophiles by four methyl groups. Ultimately, this affects the proportion of substitution products that will be created while maintaining the location of the double bond of the exomethylene isomer (1a) since S_N2' is more likely. It is also important to note that the nucleophilicity of the nucleophile and leaving group ability of the displaced halide will affect the observed reaction rate. This has implications when considering the reactivity of various nucleophiles with either chlorobutyl or bromobutyl rubber, since bromide is a better leaving group.

Guillen et al. described the stability and structure of allylic esters formed from carboxylate nucleophiles with BIIR.¹² Solution experiments conducted in toluene at 85 °C using soluble ammonium carboxylate salts have provided insight into the relationship between starting allylic bromide isomer distributions and esterification rates and product distributions.

Scheme 1.8 : Allylic Ester Formation from BIIR



Guillen's studies also revealed differences in the reactivity of allylic bromide isomers (Scheme 1.8), as BIIR samples containing a higher proportion of BrMe functionality reacted faster than "as received" rubber, which contains mostly Exo-Br. This study also showed that substitution preserves the position of the carbon-carbon double bond. By monitoring the starting allylic bromide isomer distribution and the corresponding allylic ester isomer distribution after reaction they concluded that allylic ester is formed through an S_N2 mechanism. Solvent-free work revealed that tetrabutylammonium bromide, at the time being used as a phase transfer catalyst, was also capable of promoting Exo-Br isomerization to BrMe.

The nucleophilicity of primary, secondary and tertiary alkyl amines with respect to BIIR has also been investigated under solvent-free conditions.¹³ Primary amines can be alkylated twice to give a covalent crosslinking network (Scheme 1.9).

Tertiary and secondary amines, namely N,N-dimethyloctylamine (DMOA) and Nmethyloctadecylamine, reacted with BIIR at 140°C to give E- and Z-BrMe substitution products, noting an absence of exomethylene derived structures. This was consistent with observations that N-alkylation of allylic halide by dimethylamine and trimethylamine are selective for isomerized product.¹⁴ At these elevated temperatures, there is also indication of dehydrobromination by the presence of conjugated diene structures (**2,3a,3b**). It should also be noted that tertiary amines are alkylated to form the corresponding ammonium bromide, whose aggregation in the solid state creates an ionic network of polymer chains. The reversibility of N-alkylation demanded the use of excess nucleophile to push the equilibrium toward a cross-linked state. The limits to full

Scheme 1.9 : Bis-N-Alkylation of BIIR



conversion of amine substitutions with BIIR were attributed to the reversibility of N-alkylations. The addition of excess amine can help push the equilibrium towards the N-alkylation product, however it is also important to note that excess amine can also act as a plasticizer in the elastomer.

Other work by Parent et al.¹⁶ looked more directly at the formation of ammonium and phosphonium based ionomers from BIIR. An alternative to conventional sulfur or ZnO cured thermoset elastomers is the displacement of allylic bromide by ionic functionality that can pair with sister groups on adjacent elastomer chains to form an ionic network within the material.

Aggregation of the ionic functionality and formation of an ionic network restricts the movement of adjacent polymer chains and mimics the reduction in chain mobility within the elastomer that is incurred in crosslinked materials after vulcanization.



Scheme 1.10 : Ionomer Formation

The product of N-alkylation of DMOA with BIIR produces the ammonium bromide salt shown in Scheme 1.10. As previously mentioned, these substitution reactions produce only the seemingly bromomethyl derived products. Rheological and solution viscosity tests on these materials confirmed the formation of an ionic network. Additionally, it was found that the ionomer materials exhibited similar mechanical properties to ZnO cured vulcanizates. In an attempt to increase the strength of the ionic network in ammonium based ionomers, amino alcohols were used to introduce hydrogen bonding functionality through hydroxyl groups.¹⁸ Using N,N-dimethylethanolamine to form the ammonium bromide salt resulted in an increase in the mechanical strength of the ionomer as measured by storage modulus (G'). The increase in modulus was a direct result of heightened ion-dipole interaction by polarization of the O-H bond. It should also be noted that increasing the distance of the hydroxyl group from the ion-pair by increasing the length of the aliphatic chain had no effect on the storage modulus of the materials.

Phosphonium derivatives of BIIR also show no exomethylene derived product. When compared to their ammonium counterparts, ionomers derived from the reaction of triphenylphosphine with BIIR showed much slower rates of formation. Triphenylphosphine is perhaps not as nucleophilic however it did react irreversibly forming comparable ionomers to ones derived from the ammonium based nucleophiles.

Ionomers are considered a thermoset polymer in contrast to crosslinked materials. Dissociation of the ionic groups results in breakdown of the ionic aggregation network that holds the material together. Comparatively, crosslinked materials are forever locked in their final form once vulcanized. The random distribution of isoprene within bromobutyl leads to a random and even distribution of allylic bromide during bromination and thus during the formation of ionomer by bromide displacement, a random and even distribution of charge. For this reason, ionomers also have important applications in the formation of nanocomposites. The formation and ultimately the strength of a composite rely on proper dispersion of the heterogeneous phase within the homogeneous phase of the material. Association of the additive with the randomly distributed ionic functionality within the ionomer is a good way of ensuring that the additive is evenly spread throughout.¹⁹

1.5 Catalysis of Bromide Displacement

The key to increasing reaction rates with BIIR is to increase the rate of bromide displacement by the incoming nucleophile. One must consider therefore the nucleophilicity of the nucleophile and the leaving group ability of the nucleofuge, allylic bromide. Evident from the experiments outlining the formation of allylic ester BIIR derivatives, substitution occurs more rapidly with the BrMe isomer than its Exo-Br companion. It is possible to take advantage of this enhanced reactivity by isomerizing the material such that it comprises mainly the more highly reactive BrMe isomer and exhibits overall faster substitution rates.

Nucleophilic catalysis of BIIR derivatization can be achieved by introducing a better leaving group than allylic bromide. A well-known method for increasing the reactivity of allylic halides is the Finkelstein reaction.²⁰ Reaction of an allylic halide, namely allylic chloride or allylic bromide, with NaI in acetone yields the iodinated product. While NaI remains soluble in acetone, the NaBr salt formed upon displacement of the allylic bromide is not. Precipitated NaBr removes bromide from solution and prevents reversion of the more reactive allylic iodide back to its bromide counterpart. Iodide being a better leaving group, any *in-situ* formed allylic iodide will show faster substitution rates than the allylic bromide isomers found in BIIR. Applying the Finkelstein reaction to a BIIR system is complicated by the fact that the rubber is not soluble in acetone. Other potential iodinating agents include tetrabutylammonium iodide (TBAI). Like NaI, TBAI is capable of displacing other halogens to form the iodinated product.²¹ The potential advantage of using TBAI in a BIIR system is that like TBAB, it can also promote isomerization of the material to the more reactive BrMe isomer. Nucleophilic catalysis of BIIR substitutions

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would then entail both isomerization to a more reactive allylic bromide isomer and the introduction of a better leaving group.

1.6 Research Objectives

For industrial processes and large scale production of BIIR substitution products and ionomers alike, increased rates of production are desirable. The main objective of this work is to catalyze the formation of BIIR derivatives. This has been approached in two different ways:

- 1. Exploit the difference in reactivity between the exomethylene and bromomethyl isomers in BIIR. Further referred to as Type 1 catalysis.
- 2. Increase the rate of nucleophilic substitution by introducing a better leaving group to the allylic functionality than bromide. Further referred to as Type 2 catalysis.

To meet this overall objective, the first focus of the work is to determine means by which BIIR can be isomerized. The goal here is to make the bromomethyl isomer available for nucleophilic substitution without promoting loss of HBr and conjugated diene formation.

Nucleophilic catalysis increases substitution rates through the introduction of a better leaving group than allylic bromide. This work supports nucleophilic catalysis through the introduction of allylic iodide in the place of allylic bromide. As a better leaving group and electrophile, substituting allylic iodide in the place of allylic bromide should increase substitution rates.

These isomerization strategies can then be applied to various nucleophiles. This work considers three different classes: carboxylate, phosphonium and ammonium. Ultimately the ability to catalyze substitution of any nucleophile requires knowledge of the mechanism by which the substitutions themselves take place. To determine the scope to which substitution rates can be catalyzed, the goal of this work is to gain a better understanding of the mechanisms that each class of nucleophile undergo with BIIR.

Chapter 2. Catalysis of Acetate Substitution

2.1 Introduction

Nucleophilic displacement of halide from brominated butyl rubber (BIIR) is a versatile and efficient means of producing isobutylene-based polymer derivatives. Although the sulfuration of BIIR to produce vulcanizates is the most important commercial derivatization process,²² reactions involving nitrogen, ²³ phosphorus²⁴ and oxygen²⁵ nucleophiles can be used to prepare a wide range of isobutylene-based elastomers that retain the impermeability and oxidative stability of the parent material while providing increased range of application.





The synthesis of allylic esters from BIIR and alkali metal carboxylates requires phase transfer catalysis to render the nucleophile soluble and reactive with respect to bromide displacement.²⁶ Tetraalkylammonium halides are effective in both respects, and have proven capable of

supporting solvent-free and solvent-borne alkylations of a wide range of carboxylate nucleophiles. The present study is concerned with the dynamics of homogeneous esterifications conducted in solution, with particular attention paid to differences in the reactivity of allylic bromide isomers within BIIR, and the effect of these differences on reaction rates and selectivity. This basic knowledge is used to develop nucleophilic catalysis techniques that accelerate esterification by affecting allylic halide isomer distributions and introducing superior leaving groups.

2.2 Experimental

2.2.1 Materials

Brominated 2,2,4,8,8-pentamethyl-4-nonene was prepared as described previously.⁶ The following chemicals were used as received: Bromobutyl 2030 (LANXESS Inc.), tetrabutylammonium acetate (97%, Sigma-Aldrich), tetrabutylammonium bromide (99%, Sigma-Aldrich), tetrabutylammonium iodide (98%, Sigma-Aldrich), sodium iodide (≥99%, Sigma-Aldrich), zinc stearate (Fisher Scientific), acetone (ACS, Fisher Scientific), toluene (ACS, Fisher Scientific), toluene (ACS, Fisher Scientific), chloroform-d (99.8 atom % D, Sigma-Aldrich). All reagent equivalencies were calculated on a molar basis with respect to the 0.15mmol/g of allylic bromide found in BIIR.

2.2.2 Bromobutyl Isomerization

Isomerization Using TBAB

BIIR (1g) was dissolved in toluene (19g) in a 100mL two neck round bottom flask. Once the solution was homogeneous, TBAB (0.0085g, 0.18 eq) was added. The flask was then lowered into an oil bath at 85°C and stirred using a magnet and magnetic stirrer for 240 minutes. Samples

were taken at 5, 10, 20, 30, 45, 60, 90, 120, 180 and 240 minutes and precipitated immediately in acetone. The samples were dried under vacuum to remove acetone and then re-dissolved in CDCl₃. Residual allylic bromide contents were quantified by ¹H NMR spectrum integration to an estimated 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 TBAI

BIIR (1g) was dissolved in toluene (19g) in a 100mL two neck round bottom flask. Once the solution was homogeneous, TBAI (0.0105g, 0.18 eq) was added. The flask was lowered into an oil bath at 85°C and stirred using a magnet and magnetic stirrer for 240 minutes. Tinfoil was used to mask the reaction mixture from light. Samples were taken at 5, 10, 20, 30, 45, 60, 90, 120, 180 and 240 minutes and precipitated immediately in acetone. The samples were dried under vacuum to remove acetone and then re-dissolved in CDCl₃. Residual allylic bromide contents were quantified by ¹H NMR spectrum integration to an estimated 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

BIIR (1g) was dissolved in toluene (19g) in a 100mL two neck round bottom flask. Once the solution was homogeneous, zinc stearate (0.1690g, 1.78 eq) was added. The flask was lowered into an oil bath at 85°C and stirred using a magnet and magnetic stirrer for 240 minutes. Samples were taken at 5, 10, 20, 30, 45, 60, 90, 120, 180 and 240 minutes and precipitated immediately in acetone. The samples were dried under vacuum to remove acetone and then re-dissolved in

CDCl₃ and filtered through glass wool to remove suspended zinc stearate. Residual allylic bromide contents were quantified by ¹H NMR spectrum integration to an estimated 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 Bromobutyl Reactions with Tetrabutylammonium Acetate

Reactions with "as received" BIIR

BIIR (1g) was dissolved in toluene (19g) in a 100mL two neck round bottom flask. Once the solution was homogeneous, tetrabutylammonium acetate (0.0823g, 1.78 eq; 0.1634g, 3.56 eq) was added. The flask was lowered into an oil bath at 85°C and stirred using a magnet and magnetic stirrer for 240 minutes. Samples were taken at 5, 10, 20, 30, 45, 60, 90, 120, 180 and 240 minutes and precipitated immediately in acetone. The samples were dried under vacuum to remove acetone and then re-dissolved in CDCl₃. Residual allylic bromide contents were quantified by ¹H NMR spectrum integration to an estimated 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). Allylic ester formation was monitored using δ 4.52 (E-ester, =C-CH₂-O-COR, 2H, s), δ 4.59 (Z-ester, =C-CH₂-O-COR, 2H, s), δ 5.19 (Exo-ester, CH₂=C-CH(OCOR)-CH₂, 1H, s).

Reactions with Isomerized BIIR

"As received" BIIR that contained a 90:0:10 ratio of Exo-Br:Z-BrMe:E-BrMe was isomerized as previously described using TBAB and zinc stearate. After 240 minutes at 85°C the TBAB and zinc stearate isomerized materials contained 25:65:10 and 15:40:45 ratios of Exo-Br:Z-BrMe:E- BrMe functionality respectively. These isomerized materials (0.5g) were then dissolved in toluene (9.5g) and reacted with TBAAc as previously described. Residual allylic bromide contents were quantified by ¹H NMR spectrum integration to an estimated accuracy of ± 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). Allylic ester formation was monitored using δ 4.52 (E-ester, =C-CH₂-O-COR, 2H, s), δ 5.19 (Exo-ester, CH₂=C-CH(OCOR)-CH₂, 1H, s).

2.2.4 Sodium Iodide Exchange with Brominated 2,2,4,8,8-pentamethyl-4-nonene

An excess of NaI was added to an NMR tube containing BPMN in CDCl₃. The contents were then placed in an oil bath at 45°C for 150 minutes. ¹H NMR confirmed the formation of allylic iodide. δ 3.98 (Z-IMe, =C-CH₂-I, 2H, s), δ 4.08 (E-IMe, =C-CH₂-I, 2H, s).

2.2.5 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 tetramethylsilane (TMS).

2.3 Results and Discussion

2.3.1 Dynamics of Allylic Bromide Isomerization

The exomethylene allylic bromide functionality generated by IIR halogenation is a kinetically favoured product that is susceptible to rearrangement to thermodynamically more stable E,Z-BrMe isomers. Isomerization usually proceeds by allyl bromide ionization, followed by ion-pair collapse (Scheme 2.2), and as a result, reaction kinetics are sensitive to temperature, solvent

polarity, and the presence of Lewis acids. Figure 2.1 illustrates the evolution of allyl bromide isomer distribution for toluene solutions containing 5 wt% BIIR. In the absence of catalyst, no reactivity is observed over 90 min at 85°C. However, the inclusion of 1.78 molar equivalents of Zn(stearate)₂ relative to allylic bromide resulted in substantial rearrangement. The heightened ionization of BIIR with Lewis acids is well known, and is believed to support the ZnO cure chemistry that is unique to halogenated butyl rubber. ^{27,28}

Scheme 2.2: Ionization-based Isomerization of BIIR



These data show that zinc carboxylate salts can accelerate rearrangement at 85°C without generating undesirable by-products. However, higher temperatures promote allyl cation deprotonation to form conjugated diene and HBr, whose continued reactions can severely affect molecular weight distributions if the system is not adequately stabilized with base²⁹. This restricts the useful temperature range of Zn(stearate)₂, but it is the incompatibility of Lewis acids with most nucleophiles that is severely limiting. With the objective to catalyze bromide displacements from BIIR, complications derived from the interaction of catalyst and nucleophile

are undesirable. This need for an alternate means of catalyzing BIIR isomerization has motivated an investigation of nucleophilic catalysis.



Figure 2.1 : Allylic bromide isomerization; a. Additive free; b. Lewis acid catalyzed; c. TBAB catalyzed; d. TBAI catalyzed (5 wt% BIIR in toluene, 85°C).

Bromide is the simplest nucleophilic isomerization catalyst. Indeed, allylic bromide rearrangement is rapid when BIIR is heated in the absence of an efficient acid scavenger,

presumably due to the catalytic action of eliminated HBr.³⁰ Unfortunately, dehydrobromination of BIIR under these conditions also leads to excessive polymer degradation. A viable alternative involves tetrabutylammonium bromide (TBAB), which has been shown to catalyze allylic bromide rearrangement without otherwise affecting polymer structure.²⁶ Figure 2.1c illustrates the progress of a solvent-borne BIIR isomerization conducted using 0.18 molar equivalents of TBAB relative to allylic bromide. Whereas BIIR alone is stable under these conditions (Figure 2.1a), a catalytic amount of TBAB produced a 40:60 ratio of BrMe:Exo-Br isomers after 90 min.

The E:Z isomer distribution generated by TBAB is particularly interesting. Whereas Zn(stearate)₂ accelerated BIIR rearrangement toward a 60:40 ratio of E:Z isomers (Figure 2.1b), TBAB catalyzed the formation of the Z isomer exclusively. This selectivity poses interesting mechanistic questions (it might reflect a preferential conformation of exo allylic bromide that is preserved during substitution). It also provides a simple means of gauging the relative contributions of a TBAB catalyzed isomerization process (Scheme 2.3) and an ionization-based rearrangement (Scheme 2.2).





The general catalytic scheme illustrated in Scheme 2.3 extends beyond bromide to include other charged nucleophiles such as iodide and uncharged compounds such as tertiary and secondary amines. Figure 2.1d illustrates the dynamics of BIIR rearrangement generated by 0.18 eq TBAI in dilute toluene solution. The extent of allylic bromide isomerization realized within 90 min was greater than that observed for TBAB, and nearly indistinguishable to that provided by 1.78 eq of Zn(stearate)₂.

2.3.2 Dynamics of Uncatalyzed Allylic Ester Syntheses

Toluene solutions containing 5 wt% of BIIR and small amounts of tetrabutylammonium acetate (TBAAc) are homogeneous mixtures at 85°C that react irreversibly to give the desired esters without interference from dehydrobromination and its accompanying side-reactions. Figure 2.2 illustrates the dynamics of reactions conducted at different nucleophile concentrations 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 TBAAc concentrations are listed as molar equivalents relative to the 0.15 mmol/g of allylic bromide within the polymer.

The experiments illustrated in Figure 2.2 reveal the evolution of allylic halide and ester concentrations under different reaction conditions. Figures 2.2a and 2.2b summarize reactions of "as received" BIIR that contained a 90:0:10 ratio of Exo-Br:Z-BrMe:E-BrMe. As expected for a bimolecular process, the initial rate of Exo-Br consumption generated by 3.56 eq of TBAAc (Figure 2.2b) was greater than that supported by 1.78 eq of nucleophile (Figure 2.2a). However,

Exo-Br consumption remained constant beyond the early stage of these reactions, unlike simple bimolecular substitutions that slow as reagents are consumed. A second notable feature is the



Figure 2.2 : Dynamics of BIIR esterification; a. BIIR as received – 1.78 eq TBAAc; b. BIIR as received – 3.56 eq. TBAAc; c. Zn(stearate)₂ isomerized BIIR – 1.78 eq. TBAAc; d. TBAB isomerized BIIR – 1.78 eq. TBAAc (5 wt% BIIR in toluene, 85°C).

rapid disappearance of E-BrMe functionality to give an equivalent amount of E-ester, which did not increase beyond the first sampling interval. Thirdly, Z-ester concentrations **did** increase continuously, even though Z-BrMe was absent throughout the esterification process.

Insight was gained from starting materials containing different ratios of allylic bromide isomers. Figure 2.2c shows the dynamics of a BIIR esterification that started from a 15:40:45 ratio of Exo-Br:Z-BrMe:E-BrMe functionality. Consumption of E,Z-BrMe functionality was immediate, while Exo-Br was converted slowly with dynamics comparable to an "as-received" BIIR reaction. The product isolated after 60 minutes contained a balanced E,Z-allylic ester ratio. Figure 2.2d summarizes a reaction that started from a 25:65:10 ratio of Exo-Br:Z-BrMe:E-BrMe functionality. E,Z-BrMe isomers were immediately converted, while the concentration of Exo-Br functionality declined at a lesser rate. The product obtained after 60 minutes contained a high proportion of Z-ester.

The relationship between initial allylic bromide isomer distributions and final allylic ester products is summarized in Table 2.1. In every case, final E-ester contents were equal to the E-BrMe content within the starting material, which is consistent with a simple $S_N 2$ displacement of bromide by carboxylate. In contrast, Exo-ester and Z-ester yields were variable, and depended on the concentrations of Exo-Br and TBAAc charged to the reaction. It is likely that this complexity stems from two characteristics of BIIR esterifications - the greater reactivity of E,Z-BrMe isomers relative to Exo-Br, and the ability of tetrabutylammonium bromide (TBAB) to catalyze allylic halide rearrangement.

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[TBAAc]	Initial Allylic Bromide Ratio	Final Allylic Ester Ratio
	Exo-Br:Z-BrMe:E-BrMe	Exo:Z-ester:E-ester
3.56 eq	90:00:10	45:45:10
1.78 eq	90:00:10	20:70:10
1.78 eq	15:40:45	00:50:50
1.78 eq	25:65:10	00:90:10

Table 2.1 : Initial Allylic Bromide and Final Allylic Ester Distributions^a

a. 5 wt% BIIR in toluene; 85°C; 240 min

A general mechanism that accounts for the observed dynamics is summarized in Scheme 2.1. Bromide displacement by carboxylate anion is irreversible, and proceeds through an $S_N 2$ mechanism that preserves the position and configuration of the double bond. Hence, Exo-ester is derived from Exo-Br, Z-ester is derived from Z-BrMe, and E-ester is derived from E-BrMe, with the latter two transformations occurring at much greater velocity. The by-product of all three reactions is TBAB, which catalyzes Exo-Br rearrangement to its more reactive Z-BrMe isomer. This by-product-induced activation of allylic halide supports auto-accelerating reaction dynamics that do not slow down substantially with reaction conversion in the manner of conventional $S_N 2$ reactions.

The suggested scheme involves an $S_N 2$ ' reaction of Exo-Br with bromide, but discounts an analogous $S_N 2$ ' process involving acetate. Were Exo-Br to engage TBAAc in competitive $S_N 2$ and $S_N 2$ ' processes, then the proportion of Exo-ester and Z-ester would be independent of nucleophile concentration. However, Figures 2.2a and 2.2b show that higher TBAAc concentrations increase the amount Exo-ester relative to Z-ester. This indicates that an $S_N 2$ ' reaction between Exo-Br and TBAAc must be slower than all other S_N^2 acetate alkylations, and that this potential reaction pathway can be ignored without introducing significant error to the analysis.

2.3.3 Nucleophilic Catalysis of Halide Displacement

This improved understanding of BIIR esterifications has fuelled the development of two methods of accelerating the process. The first is catalysis of Exo-Br rearrangement to generate kinetically more reactive BrMe isomers. The second is conventional nucleophilic catalysis, which renders the electrophile more reactive by introducing a superior leaving group. For the solution-borne esterifications of present interest, only the Exo-Br isomer needs to be activated.

Tetrabutylammonium iodide (TBAI) is an obvious choice for a nucleophilic catalyst, given its ability to accelerate BIIR isomerization and its reported accelerating effect on other nucleophilic substitution reactions. Figure 2.1d illustrates the effect of 0.18 eq TBAI on a dilute toluene solution of BIIR. Exo-Br rearrangement to Z-BrMe was catalyzed efficiently, such that 67% of the initial Exo-Br isomer was converted within 45 min. This is better than the TBAB process, which converted just 46% of Exo-Br to Z-BrMe under equivalent conditions. It is clear, therefore, that TBAI is an effective Exo-Br isomerization catalyst. Its potential as a conventional nucleophilic catalyst depends on its ability to generate an allylic iodide intermediate that is more reactive than equivalent bromide functionality.

Figure 2.3c contains the ¹H-NMR spectrum of the product recovered from heating a BIIR solution for 240 min with 0.18 eq TBAI. Exo-Br isomerization to Z-BrMe was extensive, and a

small singlet at δ 3.98 evolved, which corresponds to the allylic iodide product of halide exchange (Z-IMe). Its abundance increased when BIIR was heated with 20 eq TBAI, as evident from the spectrum provided in Figure 2.3b. Unambiguous characterization of both E,Z-allylic iodide isomers was gained through halide exchange of brominated 2,2,4,8,8-pentamethyl-4nonene using NaI in acetone (Figure 2.3a).



Figure 2.3 : Downfield region of ¹H-NMR spectra (CDCl₃) a. Iodinated model compound; b. BIIR exchanged with 20 eq TBAI; c. BIIR isomerized/exchanged with 0.18 eq TBAI.

The effect of 0.18 eq TBAI on a BIIR esterification is demonstrated in Figure 2.4 using plots of the iodide-catalyzed reaction and an analogous uncatalyzed process. As expected, both reactions consumed E-BrMe rapidly to generate the corresponding E-ester substitution product. The influence of TBAI on Exo-ester production was insignificant, while Z-ester yields improved sharply in the presence of iodide catalyst. This increase can be attributed to enhanced Exo-Br isomerization by iodide, as well as the potentially heightened reactivity of a Z-IMe intermediate. Similar results were observed when 1.78 eq of NaI were charged to the reaction mixture to generate TBAI *in-situ* through ion exchange with the TBAB that is liberated by esterification.



Figure 2.4 : Esterification of as received BIIR (5wt% BIIR in toluene, 2.67 eq TBAAc, 85°C).

2.4 Conclusions

The esterification of BIIR with TBAAc is auto-accelerating due to an $S_N 2$ ' isomerization of the starting material by the TBAB substitution by-product. This selective rearrangement of Exo-Br to a kinetically more reactive Z-BrMe isomer increases reaction rates and raises the yield of Z-ester relative to other product isomers. Catalytic amounts of soluble organic iodide salts also accelerate allylic bromide rearrangement, and increase BIIR esterification rates.

Chapter 3. Isobutylene-rich Ionomeric Elastomers

3.1 Introduction

The alkylation of PPh₃³¹ and tertiary amines³² by brominated butyl rubber (BIIR) generates ionomer derivatives that exhibit solid-state rheological properties, dilute solution viscosities, and NMR relaxations that are distinctly different from their parent material. Furthermore, these "onium" bromide ionomers also provide the surface adhesion that is lacking of isobutylene-rich elastomers and, as such, have been used to prepare highly reinforced clay and silica nanocomposites using simple polymer compounding techniques.³³





The solvent-free nature of these ionomer syntheses makes them ideally suited to high throughput, reactive extrusion processing. However, the dynamics of halide displacement from BIIR by PPh₃ and NR₃ have not been studied, and the relationships between allylic bromide isomer distribution and alkylation rates have not been established. Given that these nucleophilic

substitutions are accompanied by rearrangement (Scheme 3.1), knowledge of underlying reaction dynamics is needed to predict and control reaction rates and the distribution of allylic isomers amongst reaction products.

3.2 Experimental

3.2.1 Materials

The following chemicals were used as received: Bromobutyl 2030 (LANXESS Inc.), 2-[2-(dimethylaminoethoxy)ethanol] (98%, Sigma-Aldrich), tetrabutylammonium iodide (98%, Sigma-Aldrich), triphenylphosphine (99%, Sigma-Aldrich), ethyltriphenylphosphonium bromide (99%, Sigma-Aldrich), chloroform-d (99.8 atom % D, Sigma-Aldrich). All reagent equivalencies were calculated on a molar basis with respect to the 0.15mmol/g of allylic bromide found in BIIR.

3.2.2 BIIR Isomerization

Exo-Br to E,Z-BrMe rearrangement was accomplished by heating BIIR (40g) to a set-point temperature of 115°C for 120 minutes. The steady-state temperature of this process was less than 125°C.

3.2.3 Ionomer Syntheses

IIR-PPh₃Br

Elastomer (40g BIIR; 36g BIIR + 4g IIR-PPh₃Br or IIR-NR₃Br) was charged to a Haake Rheomix 600p batch mixing bowl equipped with Banbury blades at 60 rpm and at the desired temperature with 1.78 eq of PPh₃ (2.80g, 0.0109 mol). For catalyzed reactions 0.18 eq TBAI (0.395g, 0.0011 mol) was also fed into the mixer. Samples were withdrawn at 5, 10, 20, 30, 45, 60, 90 and 120 minutes and characterized by NMR. Residual allylic bromide contents were quantified by ¹H NMR spectrum integration to an estimated 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). Phosphonium bromide concentrations were quantified by ³¹P NMR spectrum integration using EtPPh₃Br as an integration standard: δ 22.2 (E-IIR-PPh₃Br, s); δ 19.8 (Z-IIR-PPh₃Br, s).

IIR-NR₃Br

Elastomer (40g BIIR) was charged to a Haake Rheomix 600p batch mixing bowl equipped with Banbury blades at 60 rpm and at the desired temperature with 3.56 eq of DMAEE (2.85g, 0.0214 mol). For catalyzed reactions 0.18 eq TBAI (0.395g, 0.0011 mol) was also fed into the mixer. To maintain consistent steady state temperatures, the rotor rpm were reduced as the reaction progressed and viscosity of the reaction mixture increased. Samples were withdrawn at 5, 10, 20, 30, 45, 60, 90 and 120 minutes and characterized by NMR. Residual allylic bromide contents were quantified by ¹H NMR spectrum integration to an estimated 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). Ammonium bromide functionality for reactions with DMEEA was monitored using δ 3.23-3.37 (E,Z-(CH₃)₂-NRBr, 6H, s).

3.2.4 Instrumentation and Analysis

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 tetramethylsilane (TMS). Reactions were conducted using a Haake PolyLab Rheocord 300p to control the temperature and a Haake PolyLab Rheomix 600p fixture equipped with Banbury blades set to 60 rpm.

3.3 Results and Discussion

3.3.1 Dynamics of PPh₃ alkylations

BIIR mixtures containing small amounts of PPh₃ are homogeneous solutions, albeit possessing viscosities and viscoelastic properties much different from small molecule solutions. Bromide displacement by PPh₃ proceeds slowly and irreversibly at 85°C, such that reaction dynamics are easily monitored (Figure 3.1). Throughout this work, concentrations of allylic and phosphonium bromide are listed as mmoles of functionality per gram of elastomer (mmol/g-XIIR), while PPh₃ concentrations are expressed as molar equivalents relative to the 0.15 mmol/g of allylic bromide that was present in the starting material.

Figure 3.1a summarizes the reaction of "as received" BIIR that contained a 90:0:10 distribution of Exo-Br:Z-BrMe:E-BrMe functionality. Despite the high Exo-Br content in this starting material, no evidence of an Exo-phosphonium bromide salt could be found by ³¹P NMR,



Figure 3.1 : Dynamics of solvent-free PPh₃ alkylations (85°C, 1.78 eq. PPh₃); a. BIIR asreceived; b. BIIR isomerized by prior heating.

meaning that $S_N 2$ displacement of Exo-Br by PPh₃ did not contribute significantly to reaction products. This is presumably due to unfavourable steric interactions between the encumbered allylic bromide and the bulky nucleophile.

The early stages of the reaction were dominated by Exo-Br rearrangement to corresponding E,Z-BrMe isomers, with only small amounts of E,Z-phosphonium bromide products appearing in the first 20 minutes (Figure 3.1a). This induction period suggests that an $S_N 2$ ' mechanism involving the direct conversion of Exo-Br to E,Z-alkylation products is not an important contributor to reaction dynamics. Appreciable alkylation rates were only observed as E,Z-BrMe concentrations rose, indicating that reaction involves simple $S_N 2$ displacements from these allylic bromide intermediates. Support for this conclusion is provided by the dynamics data illustrated in Figure 3.1b. Starting with an Exo-Br:Z-BrMe:E-BrMe distribution of 20:60:20 eliminated the induction period, and generated significantly higher PPh₃ alkylation rates. Nearly full BIIR conversion to IIR-PPh₃Br was achieved in 60 minutes.

Based on these observations, it is likely that Exo-Br is unreactive with respect to PPh₃, and that alkylation proceeds selectively through E,Z-BrMe isomerization products. Given this need for BIIR rearrangement, it is not surprising that IIR-PPh₃Br production does not follow simple bimolecular dynamics. However, the observed selectivity for the Z-IIR-PPh₃Br isomer is unexpected.

Insight was gained by studying allylic bromide isomerization in the absence of nucleophile. Figure 3.2a illustrates the evolution of allylic bromide isomers as BIIR alone was mixed at 85°C. Isomerization was evident after 30 minutes, while continuous heating for 120 minutes converted 29% of Exo-Br to a balanced ratio of E,Z-BrMe isomers. This non-selective rearrangement generates thermodynamically more stable BrMe isomers through an ionization / ion-pair collapse mechanism. While deprotonation of allyl cation intermediates can lead to dehydrohalogenation, conjugated dienes were not generated at the temperatures used throughout this work. Therefore, allylic bromide ionization contributed only small amounts of E,Z-BrMe isomers, which alkylated PPh₃ to generate corresponding E,Z-IIR-PPh₃Br functionality.

Very different behavior was observed when BIIR was compounded with 10 wt% of IIR-PPh₃Br (Figure 3.2b). Allylic bromide rearrangement was accelerated dramatically to give a high proportion of the Z-BrMe isomer, while ³¹P NMR showed that IIR-PPh₃Br functionality charged



Figure 3.2 : BIIR isomerization dynamics (85°C); a. As received; b. IIR-PPh₃Br catalyzed; c. TBAI catalyzed; d. IIR-NR₃Br catalyzed.

to the mixture was unchanged. Since this $S_N 2$ ' rearrangement conserves bromide, the process is catalytic, and will accelerate during ionomer syntheses as bromide is displaced by PPh₃ (Scheme 3.1). Since Exo-Br isomerization is necessary for PPh₃ alkylation, it follows that IIR-PPh₃Br is generated through an auto-accelerating process because the alkylation product activates the starting material. Furthermore, the observed preference for Z-IIR-PPh₃Br is a direct result of a selectivity for Exo-Br isomerization to the Z-BrMe isomer.

This knowledge has been used to develop accelerated alkylations that are more amenable to solvent-free reactive extrusion. The data plotted in Figure 3.3 illustrate two simple approaches for improving reaction velocities. Figure 3.3a shows the progress of a BIIR + PPh₃ reaction in which 10 wt% of IIR-PPh₃Br was charged to the initial mixture. This process is equivalent to a continuous alkylation process with 10% product recycle, and is designed to exploit the reactivity of the ionomer as an Exo-Br isomerization catalyst. The dynamics data show no evidence of the induction period observed in conventional reactions (Figure 3.1a), and tangible improvements in reaction economy were achieved.



Figure 3.3 : Accelerated PPh₃ alkylations; (85°C, 1.78 eq. PPh₃); a. Ionomer catalyzed; b. TBAI catalyzed.

An alternate approach to accelerating IIR-PPh₃Br production exploits organic iodide salts as nucleophilic catalysts. Figure 3.2c demonstrates the ability of tetrabutylammonium iodide (TBAI) to catalyze Exo-Br isomerization to its reactive Z-BrMe isomer. Catalytic amounts of

TBAI produced a significant effect without generating an observable quantity of allylic iodide exchange product. Nevertheless, the influence of iodide on a PPh₃ alkylation process was pronounced, with nearly quantitative BIIR conversion achieved in just 45 minutes (Figure 3.3b). It is interesting to note differences in the ability of IIR-PPh₃Br and TBAI to catalyze Exo-Br isomerization and PPh₃ alkylation. While TBAI was less reactive with respect to allylic bromide rearrangement (Figure 3.2c), it accelerated PPh₃ alkylation to a greater extent. It is likely that the reactivity of iodide is greatly enhanced when IIR-PPh₃Br is present, owing to the likelihood of anion metathesis. That is, halide exchange between TBAI and IIR-PPh₃Br can generate the corresponding IIR-PPh₃I salt *in-situ*, whose solubility and nucleophilicity within a poly(isobutylene) matrix may be improved considerably.

3.3.2 Dynamics of NR₃ alkylations

In a manner that is similar to the BIIR + PPh₃ system, the alkylation of tertiary amines under solvent-free conditions gives E,Z-ammonium bromide ionomers. However, N-alkylation is reversible in that it can be displaced by other nucleophiles. Excess amino alcohol must be added to push the equilibrium to complete allylic bromide conversion (Scheme 3.2). In practice, 2 eq of 2-[2-(dimethylaminoethoxy)ethanol] (DMAEE) is sufficient for solvent-free processes conducted at 85°C. Figure 3.4a illustrates the dynamics of such a process for "as received" BIIR. Note that the rate of Exo-Br consumption was virtually constant throughout the entire process, which is inconsistent with simple bimolecular dynamics. Furthermore, all evidence of E,Z-BrMe isomers was lost within the first sampling interval.

Scheme 3.2 : Ionomer Formation with DMEAA



The superior reactivity of E,Z-BrMe isomers with DMAEE is illustrated in Figure 3.4b, which plots the evolution of reactant and product concentrations from an initial BrMe:Exo-Br isomer ratio of 5.1:1. Conversion of BrMe functionality was quantitative within the first sampling interval, while residual Exo-Br was consumed slowly in the manner observed in the "as-received" case (Figure 3.4a). In light of the observed ability of IIR-NR₃Br to catalyze Exo-Br rearrangement (Figure 3.2d), it is proposed that NR₃ alkylations abide by the same auto-accelerating mechanism as PPh₃ reactions. That is, displaced bromide catalyzes the isomerization of Exo-Br to kinetically more reactive BrMe, which is consumed rapidly to produce more ionomer. The necessity for allylic bromide isomerization to facilitate N-alkylation is responsible for the deviation from simple bimolecular dynamics. The addition of 0.18 eq TBAI to an IIR-NR₃Br synthesis produced the expected outcome, with N-alkylation rates increased as a result of nucleophilic catalysis of BIIR isomerization and halide displacement (Figure 3.4c).



Figure 3.4 : Dynamics of solvent-free bromide displacement by 3.56 eq DMAEE at 85°C; a. BIIR as-received; b. BIIR isomerized by prior heating; c. TBAI catalyzed.

3.3.3 Optimization of a Solvent-Free Ionomer Synthesis

An economical and environmentally responsible ionomer synthesis is a solvent-free, single-stage process that converts all reagents without producing byproducts. In this context, the IIR-PPh₃Br self-catalyzed between "as received" BIIR and 1.78 eq PPh₃ is most attractive. However, the

mild conditions used to produce the data shown in Figure 3.3a cannot support a viable reactive extrusion process, owing to an excessive reaction time. Since reagent concentrations cannot be varied in a solvent-free process that seeks to convert all reagents, reaction temperature is the only variable that can be used to affect reaction velocities. Figure 3.5 illustrates a self-catalyzed IIR-PPh₃Br process operating at 120°C. The reaction was complete within 12 minutes, which is a factor of 10 faster than the analogous process run at 85°C. Further rate enhancements can be achieved by temperatures modestly higher than 120°C, but it becomes increasingly difficult to track the dynamics of such rapid processes.



Figure 3.5 : Demonstration of a practical PPh₃ alkylation; (120°C, 1.78 eq. PPh₃, 10wt% IIR-PPh₃Br).

3.4 Conclusions

Solvent-free reactions of PPh₃ show exclusivity in the formation of only BrMe derived products. It is suggested that steric interactions between the large phenyl groups and the rubber backbone prevent the formation of exomethylene derived phosphonium ionomer. Product isomer distributions show a preference for formation of the Z-BrMe derived ionomer. The apparent induction period in IIR-PPh₃Br syntheses revealed that these reactions are auto-catalytic in that the formed ionomer promotes isomerization of allylic bromide from the exomethylene isomer to the more reactive bromomethyl isomer. This is important since, as previously stated, PPh₃ does not react with Exo-Br.

Similarly, N-alkylations of BIIR with DMAEE form ammonium ionomers that are capable of isomerising allylic bromide as well. DMAEE ionomer formation occurs much more quickly than its PPh₃ analogue but is reversible, and thus requires the addition of 2 molar equivalents of nucleophile to reach full conversion of allylic bromide.

Chapter 4. Conclusions

4.1 Isomerization Dynamics

Techniques for catalyzing BIIR isomerization were studied to rearrange Exo-Br to kinetically more reactive BrMe isomers. Lewis acid catalyzed isomerization using $Zn(stearate)_2$ follows an ionization pathway that yields E- and Z-BrMe isomers in nearly equal proportions. However, its incompatibility with most nucleophiles limits the practical use of this approach. TBAB is reactive with respect to BIIR isomerization, and it does not impact negatively on the reactivity of alternate nucleophiles. This nucleophilic catalyst functions through an S_N2' mechanism, and demonstrates a clear preference for Z-BrMe isomer production. TBAI can also serve as nucleophilic isomerization catalyst, and is capable of yielding allylic iodide intermediates that are more reactive than their corresponding bromides.

4.2 Substitution Dynamics

Initial studies of the solution-borne reactions of BIIR and TBAAc system showed that the reaction was bimolecular, but overall dynamics did not fit a simple second-order rate model. This is due to the auto-accelerating nature the substitution process. Displacement of bromide by the nucleophile forms TBAB *in-situ*, which activates BIIR by catalyzing Exo-Br rearrangement to BrMe functionality. Small amounts of TBAI increased the rate of Z-ester production significantly by promoting Exo-Br isomerization and, potentially, by introducing a superior leaving group to the polymer.

Solvent-free reactions of BIIR and PPh₃ generate only BrMe-substitution products, with the inactivity of Exo-Br toward direct halide displacement attributed to unfavourable steric

interactions. This is a significant finding since industrial bromination results in an isomer distribution that lies heavily in favour of the exomethylene isomer. Similar to the TBAAc system, PPh₃ displacements are auto-accelerating in that the phosphonium bromide product catalyzes allylic bromide rearrangement. The introduction of TBAI and the use of higher reaction temperatures provided evidence of a more practical method for the formation of phosphonium bromide bromide ionomer.

Solvent-free reactions of BIIR with DMAEE are more rapid than equivalent PPh₃ alkylations, although both reactions follow similar reaction pathways. The key difference is the reversibility of N-alkylation, which demands the use of excess amino alcohol to achieve full allylic bromide conversion to ammonium ionomer.

4.3 Future Work

Further effort to characterize the microstructure of ammonium based ionomer would be beneficial, as the distribution of E,Z-isomers in this product were not monitored in this work.

Optimization of reaction conditions is required to scale up the BIIR derivatizations studied in this work. The influence of leaving groups (chloride, iodide) on the rate of halogenated butyl rubber derivatization is an important topic of study that should be considered further. Application of nucleophilic catalysis to cholorobutyl rubber is of interest. Chlorobutyl is more stable and less reactive to substitution than its brominated analogue and therefore the scope for increasing substitution rates using nucleophilic catalysis by means isomerizing the material and replacing allylic chloride with allylic iodide is encouraging.

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