LATENT AMINE CURES OF BROMINATED POLY(ISOBUTYLENE-*CO*-ISOPRENE)

by

Michael Anthony Jackson Faba

A thesis submitted to the Department of Chemical Engineering

in conformity with the requirements for the degree of

Master of Applied Science

Queen's University

Kingston, Ontario, Canada

(January, 2010)

Abstract

The allylic bromide functionality within brominated poly(isobutylene-*co*-isoprene), or BIIR, alkylates primary amines repeatedly to generate thermoset products at reaction rates that are too fast to support commercial rubber processing operations. The objective of this work was to assess the utility of latent N-nucleophiles as curatives and modification reagents for BIIR. Ideally, BIIR formulations containing these latent amines would not cure at standard compound mixing temperatures, but support high crosslinking rates and yields upon heating to conventional vulcanization temperatures.

Carbon dioxide-derived salts of ammonia, including $(NH_4)_2CO_3$, $(NH_4)HCO_3$ and $(NH_4)H_2NCO_2$, can be mixed with BIIR without incurring crosslinking at temperatures below 100°C, but they generate adequate crosslink yields upon heating to 160°C. The corresponding CO_2-derived salts of primary amines decompose below 100°C and, therefore, do not provide adequate scorch protection when mixed with BIIR. Latency was conferred on primary amines using imine derivatives, in particular N-alkylbenzaldimine and its substituted analogues. These latent curatives are activated by hydrolysis, thereby providing a means of controlling active nucleophile concentrations, and minimizing crosslinking activity at 100°C without impacting negatively on cure rates at 160^{o}C.

The scorch problems generated by primary amines extend to BIIR cure formulations employing conventional sulfur and ZnO curatives. In contrast, imine analogues are shown to provide low temperature scorch stability without impacting negatively on high temperature cure rates and extents.

Acknowledgements

First and foremost, I would like to thank my supervisor, Dr. Scott Parent, for allowing me the opportunity to work on this project. His knowledge and input were invaluable, and his drive and passion taught me many a lesson about both research and my own abilities. It is fair to say all of my experiences will come to my aid in whatever the future holds. I would also like to thank my co-supervisor, Dr. Ralph Whitney, for his generous assistance to this work, being an extra set of eyes (both in the lab and on the golf course), and for having all the answers to chemistry questions I never thought I'd have.

Thank you to all of my lab mates, past and present, for their friendship, technical support, and ability to make those long hours in the lab that much more enjoyable: Sean Malmberg, Anthony Porter, Karthik Siva Shanmugam, Shude Xiao, Adam Ozvald, Joanne McNeish, Wei Wu, Michael Kaufman, and Andrew Wong. An extra thank you to Andrea Liskova for her assistance during those times the TGA decided it wouldn't cooperate.

For all of my learning experiences outside of the lab, I have to thank Ryan, Mark, Tina, Ang, Kristen, Morgan, Ula, Jeff, Tanya, and Pedro, as well as the rest of the Empty Pitchers and Grad Club Trivia Jamboree. Special thanks to Christine, whose friendship and understanding through this entire writing process has more than once been a needed and welcome retreat.

Most importantly, thank you to my parents, Gino and Lynda. It goes without saying that none of this would have been possible without you. You never cease to be a source of inspiration, and you have allowed me the freedom to follow my dreams. Your unconditional and unwavering support through both thick and thin during my time at Queen's is and will be appreciated far more than I can ever convey. Words will never express how grateful I am. I love you both very much.

Table of Contents

List of Figures

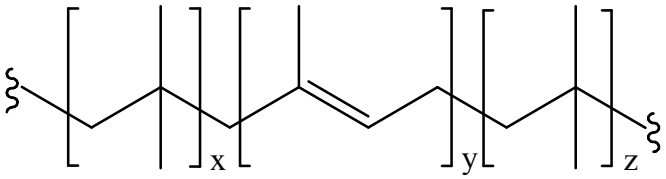
List of Tables

List of Schemes

Chapter 1: Introduction

1.1 Butyl Rubber

Poly(isobutylene-*co*-isoprene), or butyl rubber (IIR), is a random copolymer of isobutylene with 1-2 mol% isoprene (**1**). The material was first discovered in 1937 and commercially developed through the 1940s.[1] The small amount of isoprene functionality results in IIR being a valued material, as it provides the oxidative stability and gas impermeability of polyisobutylene, while including the reactive unsaturation of the isoprene subunits that can be used for cross-linking and the formation of a continuous network. This quality makes butyl rubber an ideal material for use in tire inner tube applications. Unlike most elastomers that contain a high degree of unsaturation, the low isoprene content of IIR allows for near-complete use of the reactive sites, leaving very little residual olefinic functionality in the cured material, further enhancing the resistance to oxidative or chemical degradation.[2]



1

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

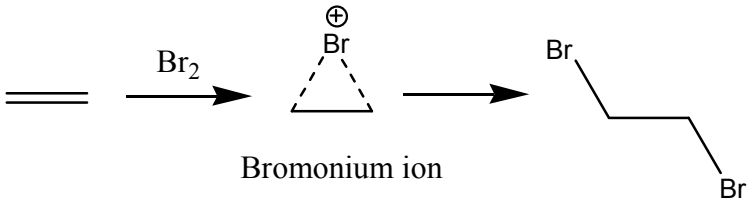
1.2 Bromination of IIR

While butyl rubber is suitable for a range of uses, it is most commonly used as a barrier material for tire applications. Note that vulcanization is required to transform all

elastomers into thermoset derivatives of adequate mechanical strength. In the case of tire inner tubes, butyl rubber vulcanization is sufficient. However, for tubeless radial tire applications, a butyl-based inner liner compound must be cured at the same temperature and for the same duration as the diene-rich elastomers that comprise the treads and sidewalls. Due to the small amount of unsaturation in butyl rubber, it cures much more slowly than these other highly unsaturated materials. Halogenation of the residual unsaturation within butyl rubber overcomes this lack of cure reactivity by introducing an allylic halide functionality that is prone to nucleophilic attack by sulfur and other curing agents. Commercially, only the chlorinated and brominated forms of butyl rubber are currently available. For inner liners, brominated butyl rubber (BIIR) has been the material of choice due to the reactivity of the brominated product being higher than that of the chlorinated product.

Exhaustive literature on small molecules has shown that olefin halogenations can occur by free radical and/or ionic pathways,[3] but where the radical mechanism is adequately suppressed, the reaction proceeds through a halonium ion intermediate. Scheme 1.1 illustrates the bromination of ethylene through a bromonium ion to give the anti addition product in greatest yield.[4] Further work by Brown and colleagues[5] using X-ray diffraction determined the bond lengths and bond angles associated with a bromonium ion of admantane.

Scheme 1.1: Bromination of Ethylene

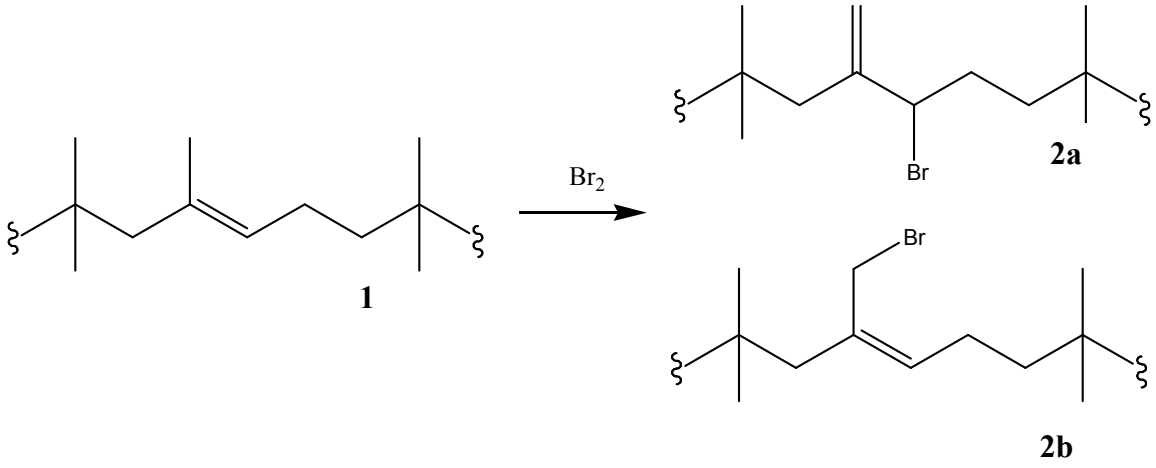


While these studies have adequately described the reactions of simple olefins such as ethylene, the characterization of butyl rubber halogenation products presents additional problems. Firstly, the amount of unsaturation in butyl rubber is very low (1-2 mol%), thereby creating challenges for standard characterization techniques such as nuclear magnetic resonance (NMR) spectroscopy. Additionally, extended relaxation times for polymers in solution lead to a broadening of NMR peaks, which adversely affects spectrum resolution. Furthermore, cured rubber samples are insoluble in the organic solvents required for solution NMR analyses.

These complications can be overcome using a model compound to mimic the reactive functionality within the polymer. The model compound that is used to study butyl rubber is 2,2,4,8,8-pentamethyl-4-nonene (PMN), the halogenation of which has been studied by Vukov.[2,6] He observed that the halogenation of PMN (and by analogy, IIR) generated two allylic substitution products: an exomethylene halide isomer, and a halomethyl isomer. The exomethylene bromide (Exo-Br, **2a**, Scheme 1.2) isomer is the kinetically favoured bromination product, representing 90% of the allylic bromide functionality within BIIR, while the bromomethyl (Endo-Br, **2b**) isomer is as the thermodynamically more stable isomer that is generated by Exo-Br rearrangement. Vukov suggested that allylic

substitution is preferred over halogen addition due to steric effects imposed by bulky isobutylene groups that surround the isoprene unit.

Scheme 1.2: Bromination of IIR



1.3 Vulcanization of BIIR

As discussed above, butyl rubber and its halogenated derivatives must be vulcanized for use in tire inner liner applications. In its uncured form, rubber is a viscoelastic material that will undergo flow when stress is applied. Vulcanization eliminates this problem by forming crosslinks between polymer chains, resulting in a polymer network of infinite molecular weight. This process increases the material's stiffness and dimensional stability by eliminating the stress relaxation processes that lead to polymer flow, thus making the material suitable for use in most industrial applications. Figure 1.2 illustrates the polymer network established by a generic vulcanization process.

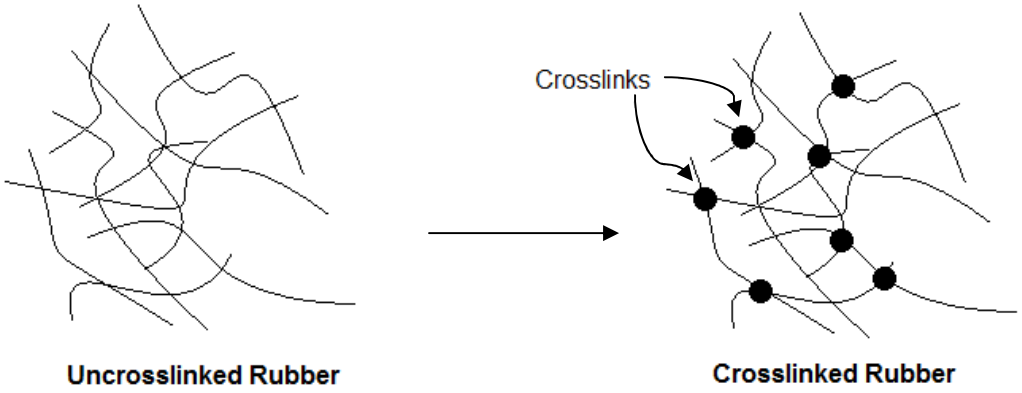


Figure 1.2 Crosslink network development through vulcanization[7]

The extent of polymer crosslinking is usually quantified using an oscillating biconical plate rheometer. These rheometers function by enclosing a sample of a rubber/curatives mixture within a cavity formed by two biconical discs, and holding this mixture at a controlled temperature. Continuous measurement of the torque required to oscillate the top fixture relative to the bottom platen provides the shear stress data needed to calculate the material's modulus. Note that the measurement of the sinusoidal stress response relative to the imposed sinusoidal strain provides the time-resolved data needed to calculate the storage (G') and loss (G") components of the dynamic modulus. Since the material properties of all viscoelastic materials, by definition, contain both a storage and loss contribution to their modulus, G* takes into account both. The simple relationship between G* and G' and G" is:

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

where, G* is the complex modulus

G’ is the storage modulus

G” is the loss modulus

The complex modulus can be additionally described as a ratio between the maximum and minimum strain and stress rates:

$$G^* = \frac{\tau_{max} - \tau_{min}}{\gamma_{max} - \gamma_{min}} \quad (2)$$

where, τ are the respective stress rates

γ are the respective strain rates

The software that accompanies modern rheometers can automatically display real-time rheological data as modulus, allowing for near immediate analysis of the state of the progressing cure, and the results can be inferred as a direct measure of crosslink density within the polymer. A standard cure curve usually contains 3 distinct regions that are of interest to rubber compounders. The first phase is the delay. In an industrial setting, this delay is vital, as it allows for the polymer to take the shape of the mold it is being held in before curing. Compounds that cure too rapidly in this stage have scorch problems.

A moderate scorch delay is followed by the curing phase of the vulcanization process, during which time the crosslink network is formed. This phase should be as short as possible to reduce overall compression molding cycle times, and to avoid possible material degradation at high temperatures. At the end of this curing period, the material must have the targeted crosslink density for end use.

The final phase of vulcanization process is dependent on crosslink network stability. The modulus can reach a stable plateau (ideal), it can continue to increase (marching modulus), or decline (cure reversion). The latter behaviour can result from the destruction of the crosslinks themselves and/or from degradation of the polymer backbone. Figure 1.3 demonstrates these areas on a standard cure curve.[8]

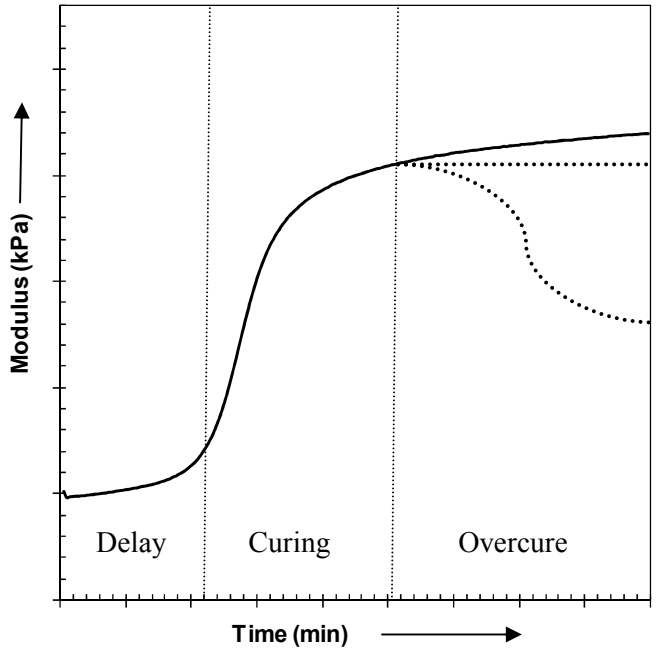


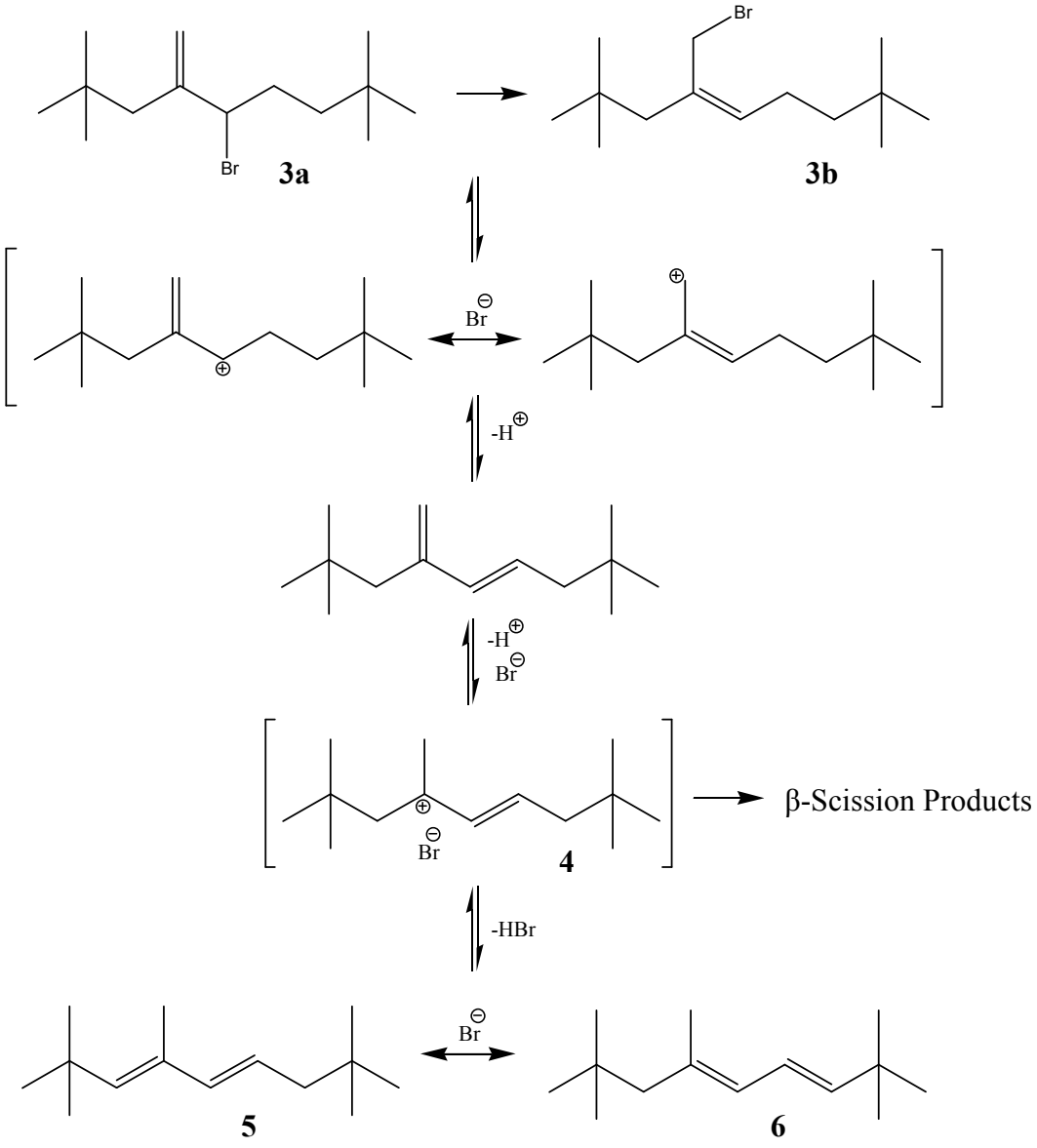
Figure 1.3 Standard Cure Curve for a rubber-based compound

1.4 Stability of Allylic Bromide and BIIR

Standard tire inner liner formulations vulcanize BIIR in the 140-170°C temperature range, which is high enough to promote allylic halide reactions other than sulfuration. Previous studies done by the Parent group have given insight on the stability of BIIR and BPMN.[9] They found that upon heating BPMN (**3a, 3b**) the molecule underwent

rearrangement from the Exo-Br isomer to the thermodynamically more stable Endo-Br or bromomethyl isomer. Moreover, it was discovered that the polymer undergoes dehydrobromination, resulting in the formation of conjugated diene structures and the release of HBr. This is summarized in Scheme 1.3.

Scheme 1.3 Thermal Stability of BPMN/BIIR

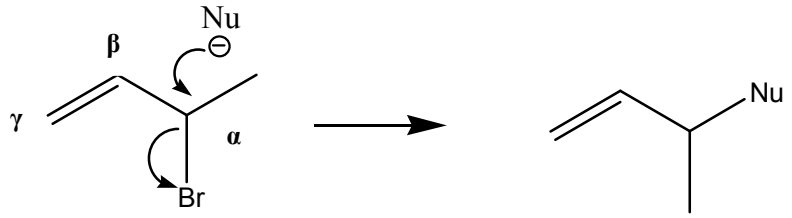


As part of their experiments, they heated a 50:50 mixture of Exo-Br and Bromomethyl isomers at 145°C. After 1 minute, the isomer ratio had adjusted to to 15:85, Exo-Br:Bromomethyl.[9] At the same time, dehydrobromination resulting in the formation of conjugated diene structures (**4**,**5**,**6**) was being observed in the NMR spectra of the sample. While this was the case with BPMN, commercially produced BIIR contains epoxides and calcium stearate to serve as acid scavengers. In the case of dehydrohalogenation of the rubber, these acid scavengers mop up the evolved HBr, thereby reducing the extent of molecular weight reduction through β-scission of allyl cation intermediates.

1.5 Nucleophilic Substitution Reactions of Allylic Bromide

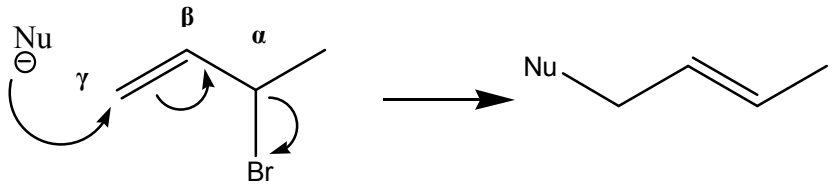
As previously mentioned, the improvement in reactivity that can be achieved through the halogenation of the isoprene unit in butyl rubber was the main reason for modifying the polymer. This increased reactivity can be used to make further derivatives of butyl by reactions with various nucleophiles. Allylic halides tend to undergo nucleophilic substitution reactions via S_N2 and S_N2' mechanisms. In the case of S_N2, the substitution occurs at the α-carbon site with loss of halide. This is outlined in Scheme 1.4.

Scheme 1.4 S_N2 Substitution Mechanism



However, as the Exo-Br isomer is the kinetically favoured product, S_N2' reactions also occur. These reactions occur with nucleophilic attack at the γ-carbon, followed by migration of the double bond.[10] This is outlined in Scheme 1.5.

Scheme 1.5 S_N2' Substitution Mechanism



In the case of BPMN, the alkyl group located off the α-carbon is a chain containing quatrenary centres. The steric bulk of this group restricts the path in which a nucleophile can take for conventional S_N2 attack. The γ–carbon is therefore, more accessible, making S_N2' preferable for Exo-Br structures.[11] In BIIR/BPMN, the Exo-Br structure is the kinetically preferred isomer. Taking this into consideration, the nucleophilicity of the attacking species, as well as that of the displaced leaving group, will have great impact on the rate of reaction, the stability of a product, or even the likelihood that a reaction will occur.

1.6 Chemical Modification of BIIR

The first and most industrially significant reaction to take place involving rubber was the accidental vulcanization of natural rubber (NR) with sulfur by Goodyear and Hancock c. 1840.[12] Since butyl rubber contains isoprene-derived unsaturation similar to that found in

NR, this process can also be applied to butyl. To this day, sulfur is primarily used as a curative in a wide variety of applications, including shoe soles, hoses, and automotive tires, the latter of which serves as the main end-use.[7] Modern tires consist of many different components and materials, but the caveat to the entire process is that they all must be cured simultaneously. As previously mentioned, the relatively low reactivity of butyl rubber is what led to the initial development of halogenated rubber. The increased reactivity of halogenated butyl, specifically bromobutyl, allows for additional nucleophiles to be used as curatives. In every case, a desirable concentration of intermolecular crosslinks needs to be achieved to meet physical property standards. It was found that, given a rubber of molecular weight 250 000, approximately 25 crosslinks per chain are needed.[12] Even at such a small amount, the network formation within the rubber would impart the desired elastic quality to the finished product. An interesting fact about BIIR is that it has the ability to cure with sulfur alone; something that no other elastomer can bring about.

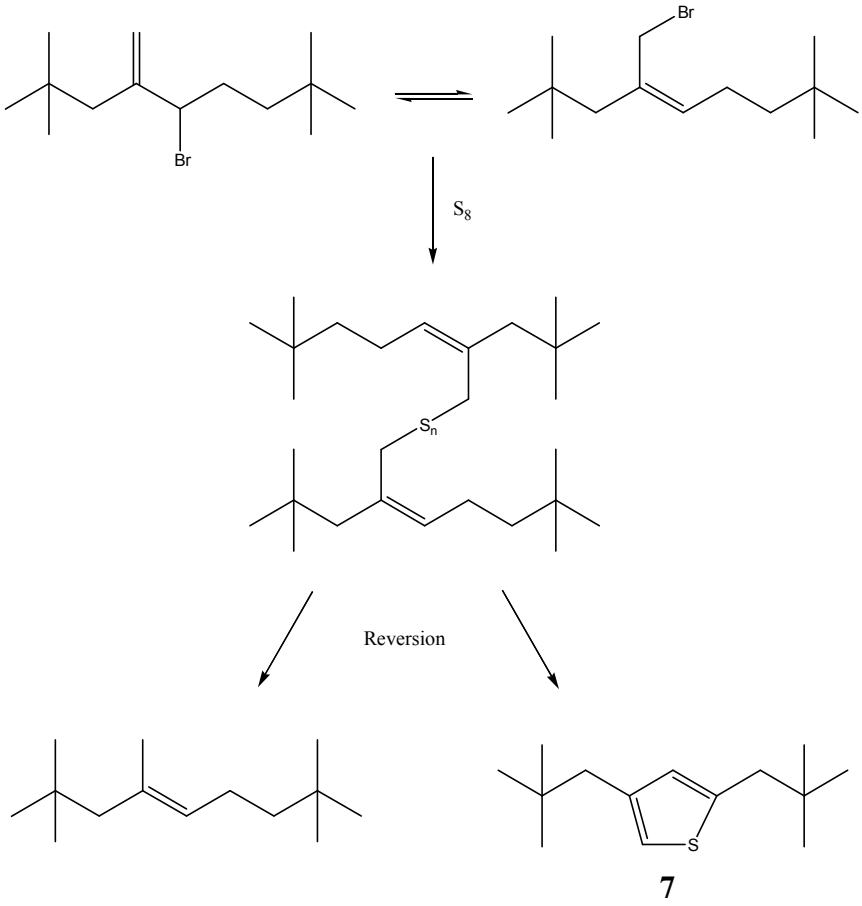
1.6.1 Sulfur

As with any vulcanization system, the difficulty in characterizing the structure of the final product means that a model compound must be used. Model compound studies of monomeric olefins have been previously investigated using 2-metyl-2-pentene.[13] Parent et al. used BPMN to study the sulfuration of BIIR.[14] They concluded that sulfuration proceeds primarily via nucleophilic substitution, with crosslinks being achieved after bis-

substitution. They also were able to determine that upon increasing the sulfur loading the sulfide crosslinks would increase in rank, achieving di- and trisulfide bridges.

A most interesting result was the observation of cure reversion products when the model vulcanization reaction was held at high temperature for prolonged periods. This behaviour was initially discussed by McSweeney and Morrison, who recognized the thermal stability of monosulfidic crosslinks, but observed the instability of crosslinks formed from disulfide and higher-rank polysulfide crosslinks.[15] This behaviour was confirmed by Parent, and a thiophene reversion product (**7**) was isolated through their model compound sulfuration study. This is summarized in Scheme 1.6. While the exact mechanism of reversion of a sulfide crosslink to thiophene is not well understood, it is thought that the reaction proceeds through interaction of persulfenyl bromides with residual olefin in the rubber. This type of behaviour has been noted previously with conventional olefins in the works of Hahn et al.[16] and Winters et al.[17]

Scheme 1.6 Sulfuration and Reversion of BIIR



7

1.6.2 Conventional Cure Acceleration

While vulcanization with sulfur provides a material with better physical properties than the uncrosslinked material, it alone does not provide optimal performance. As early as 1910, it was discovered that by adding aniline to a non-halogenated rubber/sulfur mixture, a marked increase in vulcanization rate as well as the overall material properties was observed.[18] Continuation of research in this area led to the development of a wide variety of accelerators, including many containing both nitrogen and sulfur such as sulfenamides, sulfenimides, and mercaptobenzothiazoles. These accelerators function by

forming polysulfide complexes with molecular sulfur, which in turn are more reactive than molecular sulfur itself.[19] Rather than strict reliance on S_N2 or S_N2' substitution, the enhanced reactivity of the accelerator-sulfur complex allows for easier insertion of the sulfur as a crosslink.

The most commonly studied accelerator is 2,2'-dithiobisbenzothiazole (MBTS). The interaction of MBTS with BIIR in a cure system was studied by Parent et al. as part of their sulfuration investigation.[14] With each cure accelerator, the vast majority of the chemistry that occurs takes place in an initial scorch delay period (see Figure 1.3). The length of the scorch delay varies with the accelerator type, but accelerators exhibiting longer scorch times are preferable for industrial application as this allows for maximum time to mix and mold a product before the cure is activated.

The polymer-curative-accelerator system is further complicated due to the fact that in many industrial situations there is more than one accelerator present. Binary and even higher order accelerator systems are commonplace. Additionally, filler materials and stabilizers can also impact the effectiveness of accelerators. These are the main factors behind the fact that many mechanisms of sulfur-accelerator systems are poorly understood.[18] Model compound studies have been performed in an effort to clarify the effects that accelerators can have on the crosslink network, especially in the case of sulfur. While vulcanization with free sulfur leads to a wide variety of sulfide crosslinks with varying ranks, use of accelerators tends to lead to a larger concentration of

monosulfide linkages and a higher overall number of crosslinks in general. High efficiency accelerators (accelerators with the best ability to convert sulfur into sulfidic crosslinks) result in the highest concentrations of both crosslinks, and monosulfidic crosslinks.[20]

1.6.3 Role of Zinc Oxide

As the industrial use of sulfur vulcanization increased, additional additives were included in mixing formulations to enhance the cure performance or the overall physical properties of the material. One of the most effective materials used is zinc oxide, as it was shown to both accelerate the cure and stabilize the cure from the reversion that is seen in sulfur-only formulations. Specifically, it was found that zinc oxide can undergo reactions with other accelerators in formulations. Coran studied the role of zinc in the vulcanization process as it pertains to MBTS. His research found that zinc was activated through solubilization with the MBT anion to form a salt species. This soluble zinc can then form complexes with the accelerator and undergo further reaction steps to yield a crosslink.[21] Model compound studies using cyclohexene as a natural rubber analogue led to the hypothesis that the zinc oxide-promoted mechanism proceeds through an initiation step of an ionic chain mechanism that forms activated zinc species and short-chain polysulfides.[22]

When considering halobutyl rubber, additional reaction pathways become available. The dehydrohalogenation of the rubber serves as an additional pathway through which the

zinc species becomes active by the formation of zinc halides. Many proposed mechanisms have been put forth, from Diels-Alder reactions with conjugated dienes[23] to a more widely accepted electrophilic addition mechanism involving zinc halides produced *in situ*, though even this exact mechanism is still under much debate due to the variety of active zinc species that can be formed.[23, 24,25]

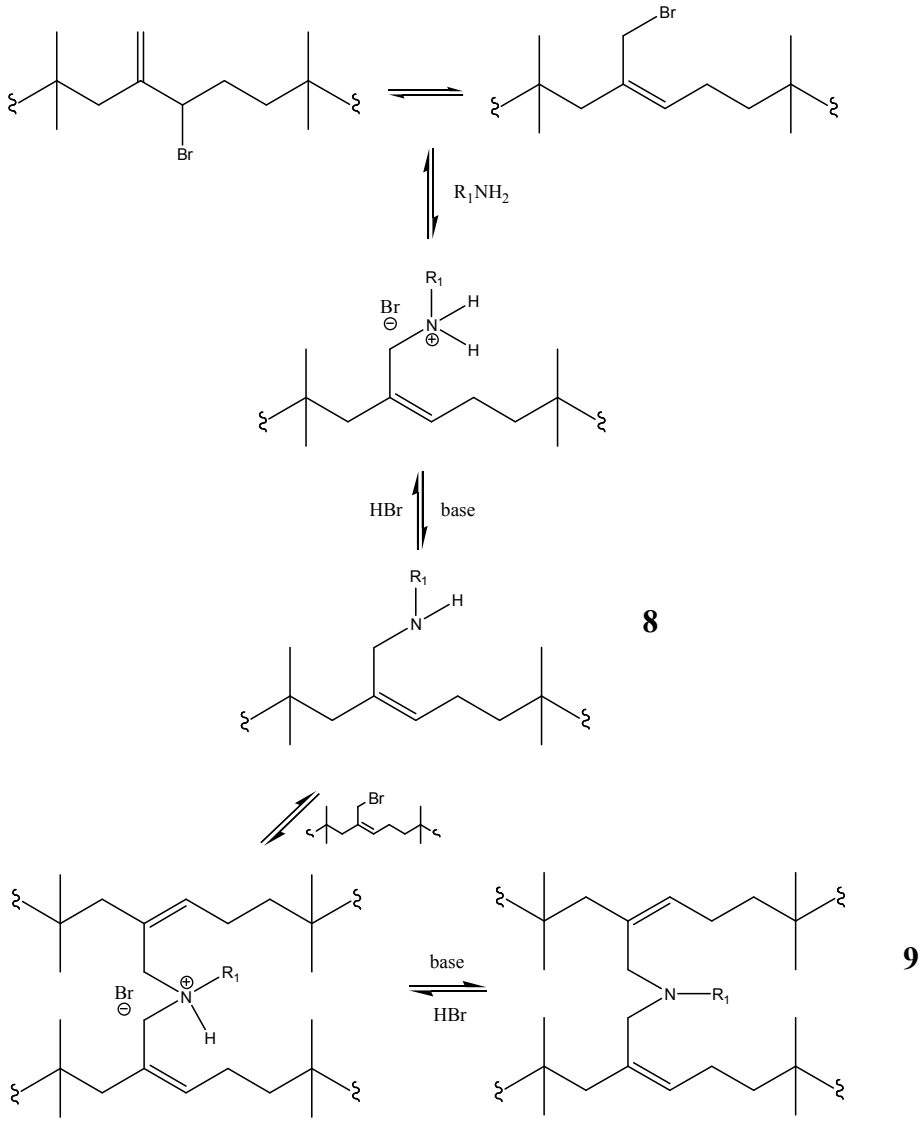
1.7 Reaction of BIIR with Amine

While current industrial cure formulations use inorganic accelerators such as zinc oxide, the first vulcanization accelerators that were discovered and used were amines.[18] Using an organic compound like an amine for cure acceleration can be beneficial, as issues such as the solubility of an inorganic compound in the polymer are not prevalent. Amines can also act as a multifunctional additive, allowing for the introduction of additional functionality to a cure network. This added functionality can be used for further reaction later on in a process, or for the compatibilization of a filler material. More recently, there is some growing concern regarding the possible impact of 'eco-toxic' zinc species present in rubber formulations, should these compounds leach out into the environment.[26]

Amines also have the ability to cure BIIR along with providing cure acceleration. Previous work conducted has determined that amines react with BIIR by N-alkylation of allylic bromide, followed by deprotonation to yield an allylic amine intermediate (**8**). As primary, secondary, and tertiary amines all have the capability to perform nucleophilic substitutions, a variety of products can be created based upon the number of times an

amine can undergo N-alkylation. Ionomers (through tertiary amine), functionalized rubbers (through secondary amine), and thermoset materials (through primary amine) are all achievable, however primary amines are the only type that can directly cure BIIR, as bis-alkylation is required to produce a crosslink (**9**). The mechanism for nucleophilic substitution of BIIR with primary amine is outlined in Scheme 1.7.[27]

Scheme 1.7 Primary Amine Substitution of BIIR



While amines, in particular primary amines, may seem like adequate cure additives they do not find widespread use in industry due to inherent scorch problems, particularly when added to conventional formulations containing sulfur. The nucleophilicity of the amine serves to ring open sulfur prematurely in the curing process, allowing for undesirable early onset of both sulfuration and N-alkylation and ultimately cure. However, the N-alkylations and subsequent proton transfers were found to be reversible, and the distribution between the reactants, ammonium bromide salt intermediates, and products is governed by thermodynamics.[27]

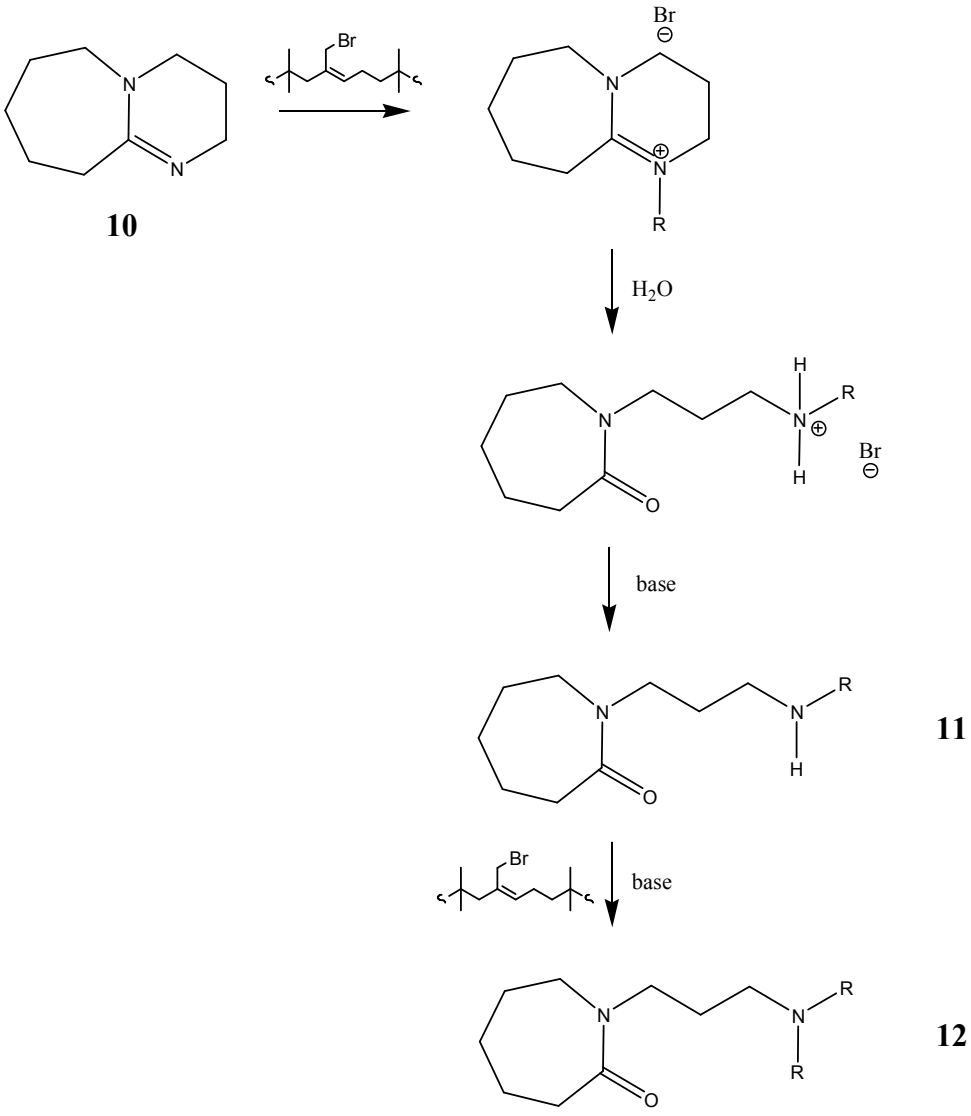
An interesting analogue to primary amine is the possibility of using ammonia in a similar nucleophilic substitution role. Ammonia is the simplest form of nucleophilic 'amine' available, and its lack of any alkyl substituents opens the theoretical possibility of four N-alkylations resulting in a quaternary ammonium salt, although steric considerations when dealing with a molecule as large as a polymer realistically reduces that number to two.

1.8 Reaction of BIIR with Bicyclic Amidine

In a similar vein to using amine, the effect of amidine bases on the stability of BIIR has been previously studied.[28] 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, **10**) is normally thought to be a strong, non-nucleophilic base, but is very effective at dehydrohalogenation.[29] Through model compound studies with BPMN, it was found that DBU is capable of curing BIIR, and it accomplishes crosslinking through a sequence of

four reactions. After initial N-alkylation, the resulting amidinium salt is hydrolyzed, ring-opening to give an amino lactam species (**11**) that functions as a conventional secondary amine. As such, the final crosslink is achieved through another N-alkylation of this amino lactam (**12**). The reactions are shown in Scheme 1.8.[28]

Scheme 1.8 N-Alkylation of DBU with BIIR



As this mechanism requires water in order to hydrolyze the amidinium salt to the amino lactam, the use of DBU can open additional applications of BIIR, as the specific curing step is latent when compared to the mechanism of a primary amine or sulfur cure.

1.9 Research Objectives

Many products have been made by curing BIIR with sulfur and a concoction of accelerator compounds for some time. Increasing focus on the impact of such products, both economically and environmentally, has prompted investigation into the potential of using BIIR with novel cure systems, creating compounds with an eye to the future. While the ability of amine to directly cure BIIR and accelerate other cures is well-established, the scorch issues that arise have limited its use in most current industrial applications. The objective of this research work is to:

1. Investigate the cure behaviour, stability, and physical properties of BIIR when exposed to primary amine.
2. Devise methods for achieving latent or delayed-onset delivery of the curative that can be easily synthesized, handled, and compounded into BIIR, and assess the performance of such compounds.
3. Investigate the ability of primary amine analogues such as ammonia and amidine (DBU) to cure BIIR.
4. Formulate delayed-onset mechanisms for these curatives as well, if needed, and assess the overall performance of these compounds.

5. Investigate the effect of the curatives studied, both standard and latent, on the acceleration of a conventional BIIR cure containing sulfur, zinc oxide, or a combination of both.

1.10 References

[1] Seymour, R.B.; *Pioneers in Polymer Science*. Kluwer Academic Publishers, Norwell U.S.A, 177-195, 1989.

[2] Chu, C.Y., and Vukov, R.; Determination of the Structure of Butyl Rubber by NMR Spectroscopy. *Macromolecules*, **18**, 1423-1430 (1985).

[3] Poutsma, M.L.; Chlorination Studies of Unsaturated Materials in Non-polar Media. III: Competition between Ionic and Free Radical Reactions during Chlorination of the Isomeric Butenes and Allyl Chloride. *Journal of the American Chemical Society*. **87**, 2172-2183 (1965).

[4] Roberts, I., and Kimball, G.E.; The Halogenation of Ethylenes. *Journal of the American Chemical Society*. **59**, 947-948 (1937).

[5] Brown, R.S, Nagorski, R.W., Bennet, A.J., McClung, R.E.D., Aarts, G.H.M., Klobukowski, M., McDonald, R., and Santarserio, B.D.; Stable Bromonium and Iodonium Ions of the Hindered Olefins Adamantylideneadamantane and Bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane. X-Ray Structure, Transfer of Positive Halogens to Acceptor Olefins, and *ab Initio* Studies. *Journal of the American Chemical Society*. **116**, 2448-2456 (1994).

[6] Vukov, R.; Halogenation of Butyl Rubber – A Model Compound Approach. *Rubber Chemistry and Technology*, **57**, 284-290 (1984).

[7] Coran, A, Y..; Vulcanization. From *Science and Technology of Rubber*, 3rd Edition, 321-364, Mark, J.E., Erman, B., and Eirich, F.R., Eds.; Elsevier Academic Press, Boston, 2005.

[8] Brown, R.; *Physical Testing of Rubber*, 4th Edition, 82-88, Springer Science, New York, 2006.

[9] Parent, J.S., Thom, D.J., White, G., Whitney, R.A., and Hopkins, W.; Thermal Stability of Brominated Poly(isobutylene-*co*-isoprene). *Journal of Polymer Science Part A: Polymer Chemistry*, **39**, 2019-2026 (2001).

[10] Magid, R.M.; Nucleophilic and Organometallic Displacement Reactions of Allylic Compounds: Stereo- and Regiochemistry. *Tetrahedron*, **36**, 1901-1930 (1980).

[11] Bordwell, F.G., Clemens, A.H., and Cheng, J.; Reactions of 9-Substituted Fluorenide Carbanions with Allyl Chlorides by S_N2 and S_N2' Mechanisms. *Journal of the American Chemical Society*, **109**, 1773-1782 (1987).
[12] Porter, M.; Vulcanization of Rubber. From *Organic Chemistry of Sulfur*, 71-118,Oae, S, Ed.; Plenum Press, New York, 1977.

[13] Lautenschlaeger, F.K.; Model Compound Vulcanization – Part I: Basic Studies. *Rubber Chemistry and Technology*, **52**, 213-231 (1979).

[14] Parent, J.S., White, G.D.F., Thom, D.J., Whitney, R.A., and Hopkins, W.; Sulfuration and Reversion Reactions of Brominated Poly(isobutylene-*co*-isoprene). *Journal of Polymer Science Part A: Polymer Chemistry*, **41**, 1915-1926 (2003).

[15] McSweeney, G.P., and Morrison, N.J.; The Thermal Stability of Monosulfidic Crosslinks in Natural Rubber. *Rubber Chemistry and Technology*, **56**, 337-343 (1983).

[16] Hahn, J., Palloch, P., Thelen, N, and H. Weidenhaupt.; Reversion Stable Networks With Polysulfide Polymers as Vulcanization Agents. *Rubber Chemistry and Technology*, **74**, 28-43 (2001).

[17] Winters, R., Heinen, W., Verbruggen, M.A.L., Lugtenburg, J., van Duin, M., and de Groot, H.J.M.; Solid-State ^{13}C NMR Study of Accelerated-Sulfur-Vulcanized ^{13}C-Labeled ENB-EPDM. *Macromolecules*, **35**, 1958-1966 (2002).

[18] Krejsa, M.R, and Koenig, J.L.; A Review of Sulfur Crosslinking Fundamentals for Accelerated and Unaccelerated Vulcanization. *Rubber Chemistry and Technology*, **66**, 376-410 (1994).

[19] Ghosh, P., Katare, S., Patkar, P., Caruthers, J.M., and Venkatasubramanian, V.; Sulfur Vulcanization of Natural Rubber for Benzothiazole Accelerated Formulations: From Reaction Mechanisms to a Rational Kinetic Model. *Rubber Chemistry and Technology*, **76**, 592-693 (2003).

[20] Lautenschlaeger, F.K, and Zeeman, P..; Model Compound Vulcanization – Part II: Comparison of Accelerators. *Rubber Chemistry and Technology*, **52**, 1030-1043 (1979).

[21] Coran, A.Y.; Vulcanization Part V: The Formation of Crosslinks in the System: Natural Rubber-Sulfur-MBT-Zinc Ion. *Rubber Chemistry and Technology*, **37**, 679-688 (1964).

[22] Wolfe, J.R., Pugh, T.L., and Killian, A.S.; The Chemistry of Sulfur Curing III: Effects of Zinc Oxide on the Mechanism of the Reaction of Cyclohexene with Sulfur. *Rubber Chemistry and Technology*, **41**, 1329-1338 (1968).

[23] Kuntz, I., Zapp, R.L., and Pancirov, R.J.; The Chemistry of the Zinc Oxide Cure of Halobutyl. *Rubber Chemistry and Technology*, **57**, 813-825 (1984).

[24] Hendrikse, K.G., and McGill, W.J.; Vulcanization of Chlorobutyl Rubber. II. A Revised Cationic Mechanism of ZnO/$ZnCl_2$ Inititated Crosslinking. *Journal of Applied Polymer Science*, **78**, 2302-2310 (2000).

[25] Hendrikse, K.G., McGill, W.J., Reedijk, J., and Nieuwenhuizen, P.J.; Vulcanization of Chlorobuty Rubber. I. The Identification of Crosslink Precursors in Compounds Containing ZnO/ZnCl2. *Journal of Applied Polymer Science*, **78**, 2290-2301 (2000).

[26] Heideman, G., Noordermeer, J.W.M., and Datta, R.N.; Multifunctional Additives for Zinc-Free Curatives for Sulfur Vulcanization. *Rubber Chemistry and Technology*, **79**, 561-588 (2006).

[27] Parent, J.S., White, G.D.F., and Whitney, R.A.; Amine Substitution Reactions of Brominated Poly(isobutylene-*co*-isoprene): New Chemical Modification and Cure Chemistry. *Macromolecules,* **35**, 3374-3379 (2002).

[28] Whitney, R.A., Penciu, A, Parent, J.S., Resendes, R, and Hopkins, W.; Cross-Linking of Brominated Poly(isobutylene-*co*-isoprene) by N-Alkylation of the Amidine Bases DBU and DBN. *Macromolecules*, **38**, 4625-4629 (2005).

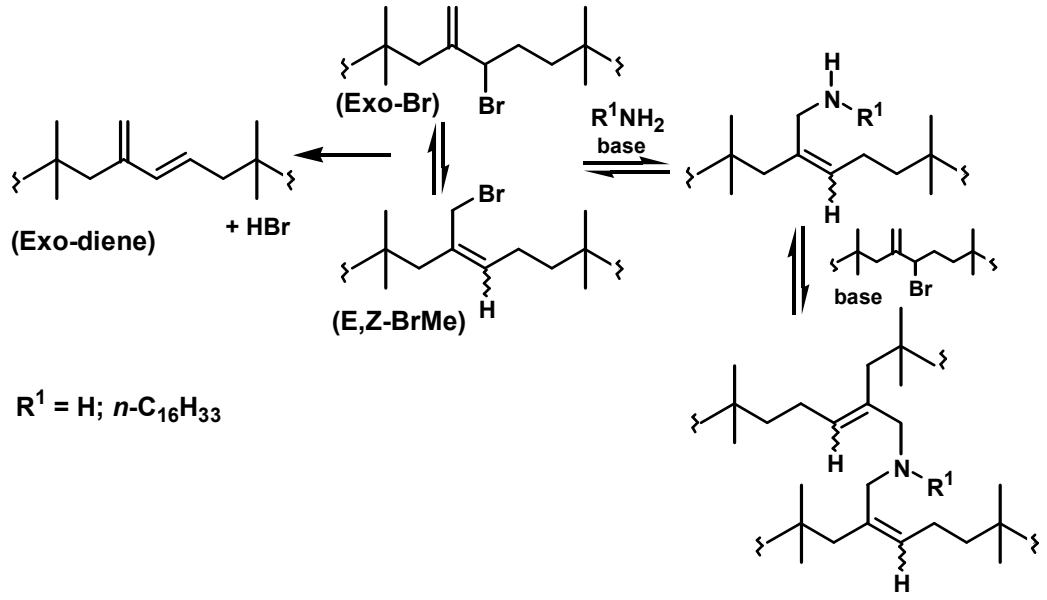
[29] Oediger, H., Moeller, F., and Eiter, K.; Bicyclic Amidines as Reagents in Organic Syntheses. *Synthesis*, **11**, 591-598 (1972).

Chapter 2: CO_2-Derived Delayed Onset Nitrogen Nucleophiles

2.1 Introduction

A wide range of isobutylene-based elastomers are accessible through halide displacement from brominated poly(isobutylene-co-isoprene) (BIIR). Nitrogen based nucleophiles, including ammonia, amines and amidines are highly reactive under solvent-free conditions, giving a range of thermoset, functional and ionomer derivatives. Rheological and model compound studies of the BIIR + primary amine system have provided insight into these high-temperature N-alkylations, the details of which are summarized in Scheme 2.1.

Scheme 2.1 N-alkylation of BIIR with Primary Amine



A typical grade of BIIR contains on the order of 0.15 mmole/g of allylic bromide functionality in the form of an exomethylene isomer (Exo-Br). This kinetically preferred

bromination product isomerizes readily to thermodynamically more stable E,Z-BrMe isomers, with temperatures on the order of 130°C promoting rearrangement as well as HBr elimination to conjugated diene.[1] Amine bases do not accelerate this E1 elimination, but displace bromide to give mono- and bis-N-alkylation products[2]. The substitution and proton transfers involved in this cross-linking process are reversible, leading to an equilibrium distribution of reaction products.

The N-alkylation of primary amines under solvent-free conditions proceeds quickly at the temperatures that develop during BIIR compounding. Therefore, the usefulness of this chemistry would be improved if nucleophile delivery could be controlled such that compounds can be mixed without concern for premature cross-linking. This has led us to examine latent forms of N-based nucleophiles that are easily handled and can be activated by moisture and/or heat when desired. Whereas the dynamics of simple bromide displacements follow bimolecular substitution kinetics, a latent nucleophile can provide additional degrees of freedom to those interested in exploiting N-alkylation chemistry. Latent nucleophiles that are thermally activated can support vulcanization processes that do no suffer from scorch safety issues, while latent forms that are hydrolytically sensitive may support products intended for moisture-curing applications.

In this section, the utility of the CO_2-based salts of organic nitrogen nucleophiles are evaluated as delayed-onset curatives. The studies start with a brief examination of the ammonia system before progressing to latent primary amines and amidines.

2.2 Results and Discussion

2.2.1 Latent Sources of Ammonia

The cross-linking of BIIR with nitrogen nucleophiles involves alkylation by allylic bromide, followed by deprotonation of the resulting ammonium bromide salt to give an allylic amine intermediate (Scheme 2.1; R^1=H). Subsequent N-alkylation/deprotonation gives the desired thermoset product. The use of excess ammonia is the simplest means of introducing base to the system, but the volatility of ammonia complicates its direct use in BIIR compounding. A practical, latent source of ammonia that is cure-inactive at 100°C, but supports cross-linking at 160°C, is desirable.

Carbon dioxide-derived salts of ammonia are inexpensive reagents that decompose thermally to liberate ammonia, CO_2 and water in proportions that are dictated by salt composition. While ammonium carbonate ($(NH_4)_2CO_3$), ammonium bicarbonate ($(NH_4)HCO_3$) and ammonium carbamate ($(NH_4)H_2NCO_2$) have significant vapour pressures, they are easily handled as solids, and can be compounded with BIIR without difficulty. The rheometry data presented in Figure 2.1 show that, irrespective of the number of molar equivalents of $(NH_4)_2CO_3$ relative to the allylic bromide functionality within BIIR, the storage modulus evolves slowly over a 20 min period at 100°C. Curing was rapid when these samples were heated to 160°C, giving transparent thermoset products that were free of voids/bubbles. That CO_2 evolution had no effect on product appearance is due to the relatively small amount of salt needed to cross-link the elastomer, and the high pressure imposed during the compression-molded curing process.

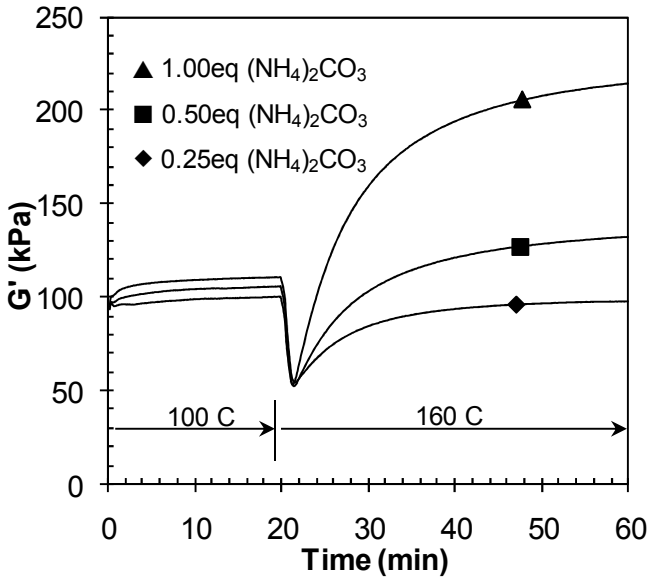


Figure 2.1: Storage modulus of BIIR + $(NH_4)_2CO_3$ formulations

Cross-link densities, as revealed by the final storage modulus (G') of a cured product, were sensitive to the amount of salt charged to the system. In theory, ammonia can be N-alkylated as many as four times. However, steric effects imposed by bulky polymer chains make it unlikely that the reaction will progress beyond a bis-alkylation product. Therefore, only one-half an equivalent of NH_3 relative to allylic bromide should meet the stoichiometric amount needed to convert all curing functionality into cross-links. The data illustrated in Figure 2.1 show that one equivalent of $(NH_4)_2CO_3$ generated the highest cross-link density of the tested formulations, which suggests that ammonia is serving as both a nucleophile and a base, the latter acting to deprotonate allyl ammonium bromide intermediates such that multiple N-alkylations can occur (Scheme 2.1).

Insight was gained by thermogravimetric analysis of $(NH_4)_2CO_3$ dispersed in an inert polyisobutylene matrix (Figure 2.2a). Although the reported decomposition temperature

for pure $(NH_4)_2CO_3$ is 23°C, the **observed** onset of mass loss for the salt in polyisobutylene was 55°C. The difference is attributed to matrix impermeability, which retards the release of NH_3, CO_2, and water. Polyisobutylene is valued commercially for its low gas permeability, and its ability to hinder the loss of ammonia is particularly useful in the present context, since salt decomposition is very likely to occur while mixing the compound, and will be quantitative at the lower temperature limit of 100°C.

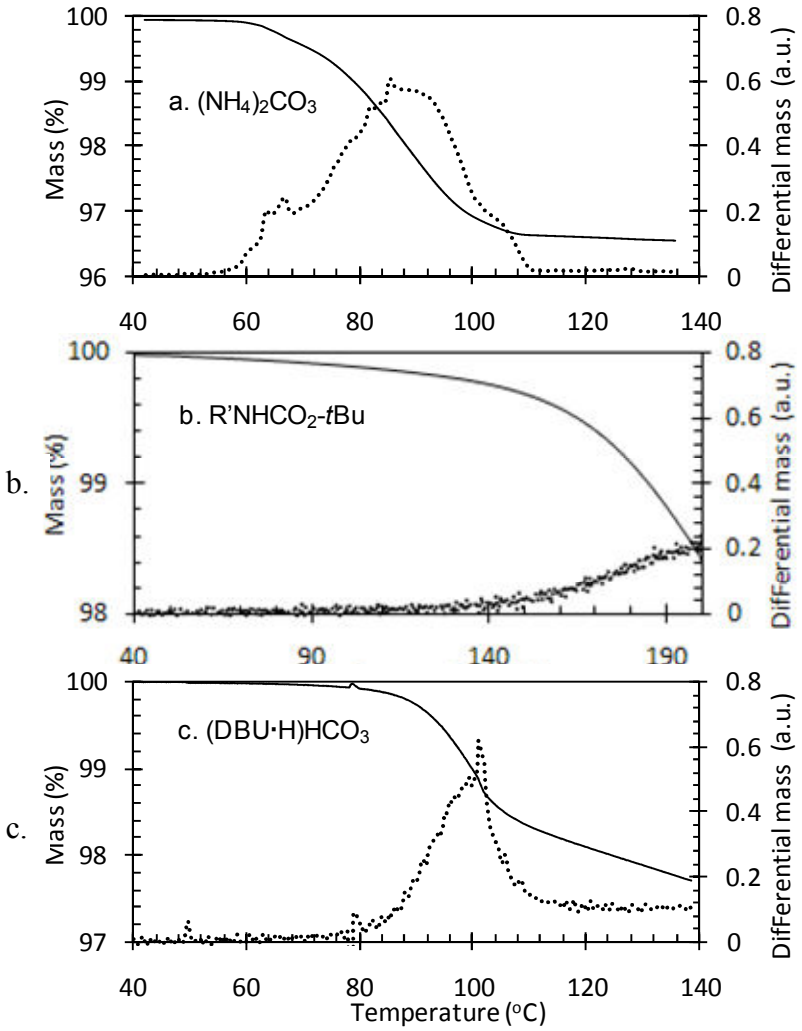


Figure 2.2: Thermogravimetric analysis data for $(NH_4)_2CO_3$, $C_{16}H_{33}NHCO_2$-tBu, and $(DBU{\cdot}H)HCO_3$ decomposition in poly(isobutylene).

Given the thermal instability of $(NH_4)_2CO_3$, the inactivity of its cure formulation at 100°C is attributed to the slow progression of the repeated N-alkylation/deprotonation reactions between BIIR and released ammonia. The data presented in Figure 2.3 confirm that prolonged heating of a $(NH_4)_2CO_3$ formulation to 100°C will cross-link BIIR, and that higher temperatures will increase reaction rates to the point that full cure can be reached within 30 min at 160°C. Therefore, $(NH_4)_2CO_3$ is a convenient means of delivering ammonia as a BIIR curative, with low temperature scorch protection resulting from low kinetic reactivity as opposed to the intrinsic stability of the latent nucleophile.

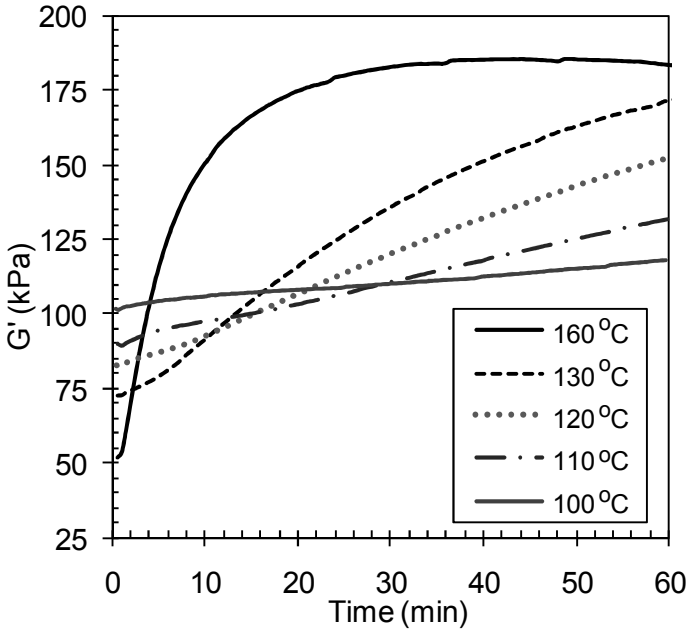


Figure 2.3: Storage modulus of BIIR + 1.0 eq $(NH_4)_2CO_3$ at different cure temperatures.

Comparison of the cross-link densities established by ammonium carbonate, bicarbonate and carbamate revealed only minor differences when equivalent amounts of latent ammonia were charged to the formulation (Table 2.1). In general, $(NH_4)_2CO_3$ and $(NH_4)H_2NCO_2$ provided very consistent cure performance, while the $(NH_4)HCO_3$ system

was more erratic, presumably due to difficulty in dispersing the higher salt loadings that were needed to meet the ammonia equivalent targets.

Table 2.1 Modulus and TGA Summary of CO_2-derived Curatives

			G'_{max} at 160°C	
	T_{dec} (°C)	T_{dec} (PIB;°C)	0.5 eq. (kPa)	1.0 eq. (kPa)
$(NH_4)_2CO_3$	23	59	133	215
$(NH_4)HCO_3$	32	69	178	227
$(NH_4)H_2NCO_2$	21	60	161	191
$C_{16}H_{33}NH_2$	---	---	225	294
$(R^1NH_3)HNR^1NCO_2$	60	69	208	251
R^1NHCOO-*t*-Bu	130	146	49	67
DBU	---	---	243	319
DBUH·HCO_3	64	75	127	255

2.2.2 Latent Sources of Primary Amines

1-Hexadecylamine ($C_{16}H_{33}NH_2$) melts at 45°C to give a liquid that mixes efficiently into BIIR within conventional polymer processing equipment. However, it is alkylated repeatedly by allylic bromide even at mild temperatures, leading to BIIR gelation when compounds are stored for prolonged periods. Furthermore, the extent to which $C_{16}H_{33}NH_2$ cures BIIR at 100°C was excessive. Maintaining a compound containing 1.3 molar equivalents of amine to allylic bromide for 20 min at this temperature gave a thermoset with a storage modulus of 141 kPa (Figure 2.4). Subsequent heating to 160°C increased the cross-linking rate while bringing the modulus to an ultimate value of 296 kPa. Note that this is comparable to that generated by the ammonia+CO_2 formulations (Table 2.1).

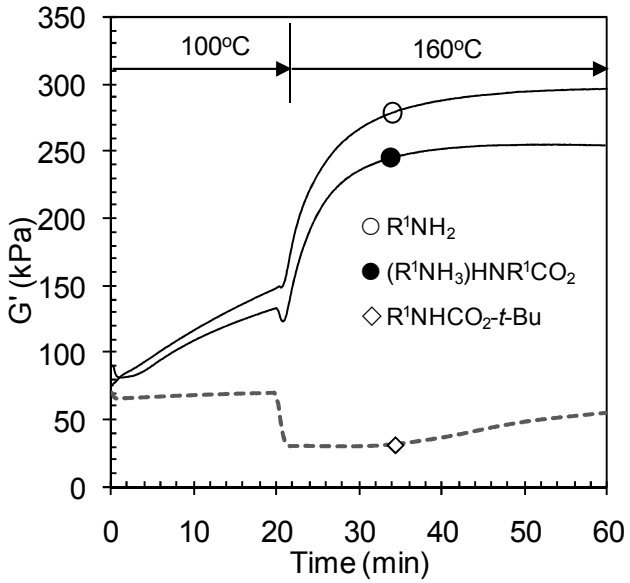


Figure 2.4: Storage modulus of BIIR + 1.3 eq $C_{16}H_{33}NH_2$, $(R^1NH_3)R^1NHCO_2$, R^1NHCO_2-*t*-Bu.

A straightforward extension of the latent ammonia chemistry uses CO_2-derived salts of primary amines. The reaction of amines and CO_2 is industrially useful in applications such as natural gas purification,[3] chemical synthesis,[4] and sequestration to control greenhouse gas emissions. Alkylammonium alkylcarbamates have also been investigated for their ability to act as gelation agents for use in reversible ionic aggregation and assembly applications.[5] It was found that the carbamate salt of hexadecylamine could be mixed into BIIR at 50°C without affecting the compound's modulus, but heating to 100°C produced a cure profile very similar to that generated by free amine (Figure 2.4). This failure to meet the delayed-onset cure criterion stems from a low temperature of salt decomposition, and the high reactivity of primary amines with respect to BIIR. TGA revealed an initial weight loss at 70°C, meaning that this carbamate salt will release

$C_{16}H_{33}NH_2$ in the very early stages of a 100°C cure. This decomposition temperature through TGA analysis is supported by the work of Holas et al.[6]

An alternate approach involves carbamate ester decomposition. Protecting an amine through formation of a carbamate ester has been previously used for surface modification.[7] Reaction of $C_{16}H_{33}NH_2$ with di-*tert*-butyl dicarbonate yields the corresponding t-butyl ester, R^1NHCOO-*t*-Bu, which decomposes at 130°C to yield amine, CO_2 and isobutylene (Figure 2.2b). The rheology data presented in Figure 2.4 confirm that this reagent does not cure BIIR at 100°C. A prolonged induction period is also observed at 160°C as thermolysis of the carbamate ester progresses. Unfortunately, ultimate cure extents are low, owing to the loss of allylic bromide functionality to dehydrohalogenation. Additionally, the decomposition of the carbamate ester results in liberation of isobutylene, forming bubbles in the vulcanizate. This can lead to reduced mechanical performance of the material. Note that heating BIIR alone to 160°C converted 19% of allylic bromide to conjugated diene within 10 min, and 43% was converted after 20 min. If the amine nucleophile is not present to convert allylic bromide to N-alkylation products, then electrophile decomposition will impact negatively on reaction yields. It would appear, therefore, that the 130°C thermolysis temperature of R^1NHCOO-*t*-Bu is too high to support an efficient BIIR crosslinking process.

2.2.3 Cyclic Amidine Precursors

Although cyclic amidine bases such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) are often said to be non-nucleophilic, they support rapid and efficient BIIR cures. DBU is

described as being a strong base able to promote dehydrohalogenation without side reactions.[8] This behaviour makes DBU a candidate for thermoset formation. Previous model compound and rheological studies have shown that DBU is stable to hydrolysis, but highly susceptible to alkylation[9] (Scheme 2.2). Studies have found that the resulting amidinium ion hydrolyzes readily to give an aminolactam intermediate,[10] which displaces bromide from BIIR to give a thermoset product. The cure dynamics of the BIIR + DBU system are illustrated in Figure 2.5, which demonstrate the rapid rate of G' growth at 100°C, and the high ultimate state of cure realized upon heating to 160°C. The water content of BIIR is typically insufficient to support complete ring opening, necessitating the use of a water releasing component such as $CaSO_4 \cdot 2H_2O$ (gypsum). The addition of 1.3 eq of gypsum raised the final modulus 25% to a value of 318 kPa.

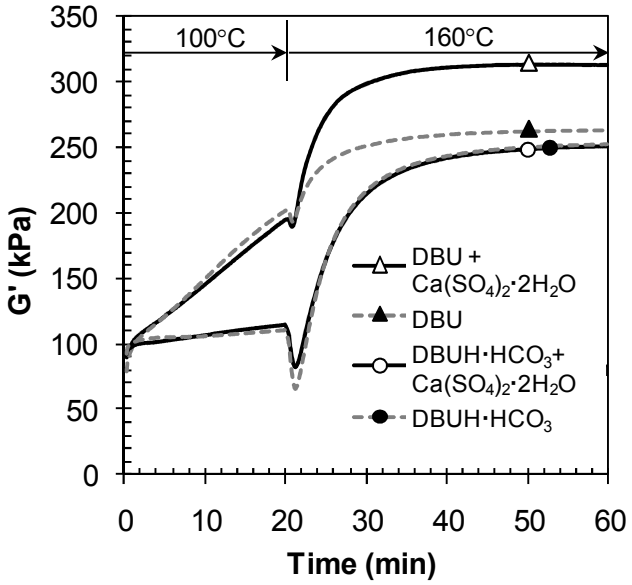
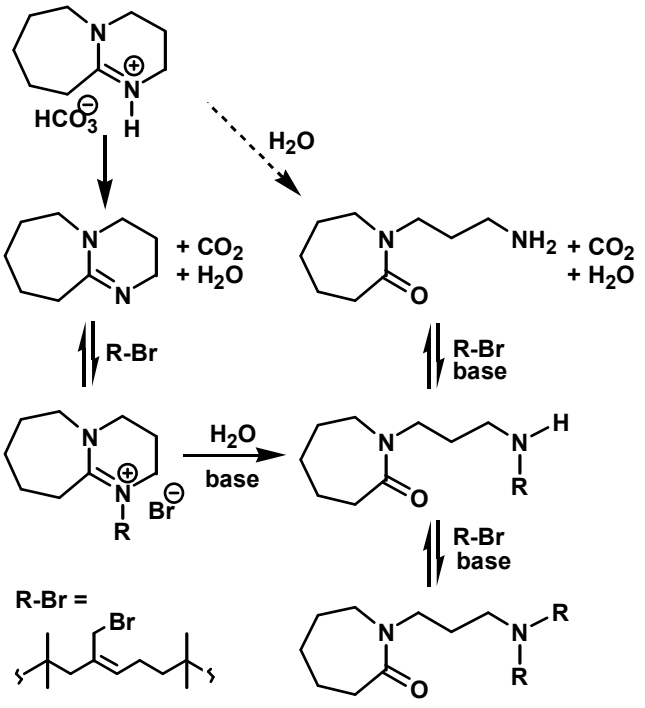


Figure 2.5 Storage modulus of DBU and $DBUH \cdot HCO_3$ salt formulations (1.3 eq nucleophile and $CaSO_4 \cdot 2H_2O$).

Transforming DBU into a latent curative requires contacting it with a wet stream of CO_2 to yield a bicarbonate salt[11,12] that decomposes at temperatures above 64°C (Figure 2.2c), a practice first used for reversible CO_2 recovery from industrial waste gas.[13] As a result, this solid can be dispersed in BIIR at 50°C, and does not cross-link the polymer substantially when maintained at 100°C (Figure 5). Raising the temperature to 160°C brings the storage modulus to the levels observed for primary amines and ammonia, but significantly below that recorded for a free DBU formulation.

Scheme 2.2. N-alkylation of DBU with BIIR through (DBU•H)HCO_3



Insight into the nature of a DBU-bicarbonate cure was gained by heating the salt with gypsum in a toluene solution. The predominant decomposition product was DBU, with evidence of a small amount of what is likely to be a primary aminolactam[2,10] (Scheme 2.2). However, the yield of this uncharacterized DBUH·HCO_3 hydrolysis product was

less than 10%, and this side reaction is unlikely to account for the lower cross-link densities recorded for the salt. This suggests that the insolubility of DBUH·HCO_3 is a contributing factor, since salt decomposition in a dispersed phase must be followed by diffusion into the BIIR matrix and reaction with allylic bromide. This is in sharp contrast to the free DBU system where the amidine is completely soluble and, hence, readily available as both nucleophile and base.

While the bicarbonate salt does not provide the crosslink density of free DBU, it does provide an additional advantage, in that its decomposition releases water, thereby eliminating the need for gypsum. Indeed, the cure dynamics generated by DBUH·HCO_3 were unaffected by the addition of $CaSO_4$·$2H_2O$, as shown in Figure 2.5.

2.3 Conclusions

Reactions involving nitrogen-based nucleophiles and allylic bromide functionality in BIIR can result in a wide range of thermoset and ionomer materials that can be useful for industrial applications. However, many of these compounds react readily with allylic bromide and introduce scorch problems at industrial working temperatures. Ammonia in the form of a CO_2 salt such as ammonium carbonate showed a moderate cure of BIIR with scorch stability at 100 ^oC. TGA analysis revealed that the salt decomposes readily below 100 ^oC, therefore the stability is a result of solubility and kinetic considerations of ammonia within the rubber. While attempts to synthesize a CO_2-derived salt of a primary amine were successful, the cure behaviour of this salt showed inadequate scorch protection at 100 ^oC. This was due to a relatively low salt decomposition temperature of ~60 ^oC. Protecting the primary amine with a *tert*-butyl carbamate ester significantly

raised the decomposition temperature above 100 ^{o}C, however this made the molecule too stable for the purpose. Decomposition was not achieved until ~130 ^{o}C, well after dehydrobromination of the rubber had begun, reducing the amount of available electrophile for crosslinking and ultimately resulting in unsatisfactory cure. The use of an amidine, DBU, resulted in an easily formed bicarbonate salt whose cure behaviour showed relative stability at 100 ^{o}C, but a high degree of activity at 160 ^{o}C. A moderate cure was achieved, however to a level below that of a free DBU cure formulation. The proposed reason for this is due to the solubility difference of non-polar free DBU and its polar bicarbonate salt in non-polar BIIR, as free DBU would be much more available to serve as a nucleophile and base to achieve cure.

2.4 Experimental

Materials. Ammonium carbonate (30% ammonia), ammonium bicarbonate (99%), ammonium carbamate (99%), 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, 98%), 1-Hexadecylamine (technical grade, 90%), di-*tert*-butyl dicarbonate (99%), and calcium sulfate dihydrate (gypsum, 98%) were used as received from Sigma Aldrich (Oakville, Ont.). Ethyl ether (ACS, anhydrous), methylene chloride (ACS), acetonitrile (HPLC grade), and magnesium sulfate (anhydrous) were used as received from Fisher Scientific. Hexanes (ACS) were used from Caledon Laboratory Chemicals (Georgetown, Ont.) and dried with Molecular Sieves Type 3A from BDH Inc (Toronto, Ont.). CO_2 (BOC, Bone Dry Grade 2.8, 99.8 %) and nitrogen (BOC) were used as received. BIIR (LANXESS BB2030, $M_n \approx 400{,}000$ g/mol, allylic bromide content ≈ 0.20 mmol/g) was used as

supplied by LANXESS Inc. (Sarnia, Ont.). Polyisobutylene (PIB, $M_w \approx 85{,}000$ g/mol) was used as received from Scientific Polymer Products (Ontario, New York).

Synthesis of Amine Carbamate Salt. 1-Hexadecylamine (0.655 g, 2.7 mmol) was charged into a round-bottom flask with stir bar. The flask was placed under a vacuum and back-filled with N_2. 30 mL of dry hexanes were added into the flask via syringe, and the mixture was allowed to mix for 15 minutes. The hexanes were dried under inert N_2 atmosphere with Molecular Sieves, Type 3A. Upon solution formation, bone dry CO_2 was bubbled into the flask for 45 minutes. The resulting white precipitate was taken and vacuum filtered with 3 hexanes washes (3 x 5 mL).

Synthesis of DBU Bicarbonate Salt. DBU (4.6 g, 0.03 mol) was charged into a flask with 6 mL of acetonitrile. CO_2 was fed through a water bubbler, and bubbled into the flask for 30 minutes. The resulting white precipitate was taken and vacuum filtered with 3 x 5mL acetonitrile rinses. ^{1}H NMR spectra in $CDCl_3$ were obtained using an Avance Bruker 500 MHz spectrometer. The broad singlet at 5.45 ppm suggests that the cation was protonated at the amidine nitrogen, as shown in Scheme III.

DBU Bicarbonate Salt: (500 MHz, $CDCl_3$): ^{1}H δ (ppm) = 5.45 (1 H, br s, NH), 3.30 (2H, t, N-CH_2), 3.24 (4H, m, N-CH_2, =N-CH_2), 2.49 (2H, d, CH_2), 1.82 (2H, m, CH_2), 1.66 (4H, br d, CH_2), 1.57 (2H, br d, CH_2).

Synthesis of *t*-butyloxycarbonyl (*t*-BOC) protected hexadecylamine. 1-hexadecylamine (5.25 g, 0.22 mol) was charged into a flask with 50 mL methylene

chloride. Di-*tert*-butyl dicarbonate (5.0 g) was added, along with 40 mL of 0.6 M solution of $NaHCO_3$ in H_2O and 3.85 g NaCl. The solution was refluxed for 3.5 hours. The reaction mixture was washed with 2x 25 mL of ether. The collected organic extracts were dried with anhydrous magnesium sulfate and filtered. The ether was removed by rotary evaporation, and the resulting white precipitate was air dried.

t-BOC protected hexadecylamine: (600 MHz, $CDCl_3$): ^1H δ (ppm) = 4.48 (1 H, br s, NH), 3.09 (2 H, m, R-CH_2-N), 1.43 (9 H, s, C-CH_3), 1.24 (28 H, m, -CH_2-), 0.87 (3 H, t, -CH_3).

Thermogravimetric Analysis of Ammonium Salts. Thermogravimetric analysis (TGA) of each ammonium salt was performed using a TA Instruments Q-Series TGA 500. All samples were run in platinum pans, using nitrogen as the purge and sample gas, with flows of 40 mL/min and 60 mL/min, respectively. Samples of 10-20 mg were first ramped from 20-200 ^oC at a rate of 5 ^oC/min, and held at 200 ^oC for 10 minutes. Pure salts were analyzed, as well as 4.5 wt% samples of the salt in polyisobutylene ($M_w \approx$ 85,000).

Delayed Onset N-alkylations with Hexadecylamine and its Carbamate salt. BIIR (40 g) was mixed with hexadecylamine or its carbamate salt (1.3 eq to allylic bromide) in a Haake Rheomix 600 batch mixer equipped with Banbury blades at 60 rpm and 50 ^oC for 10 min. Aliquots of the resulting masterbatch (5 g) were charged to an Advanced Polymer Analyzer (Alpha Technologies) operating with 3 degrees of arc at a frequency of 1 Hz.

Delayed Onset N-alkylations with DBU. BIIR (40 g) was mixed with DBU or its bicarbonate salt (1.3 eq to allylic bromide) and calcium sulfate dihydrate (gypsum, 1.3 eq to allylic bromide) in a Haake Rheomix 600 batch mixer equipped with Banbury blades at 60 rpm and 50°C for 10 min. Aliquots of the resulting masterbatch (5 g) were charged to an Advanced Polymer Analyzer (Alpha Technologies) operating with 3 degrees of arc at a frequency of 1 Hz.

Delayed Onset N-alkylations with *t*-BOC protected amine. BIIR (40 g) was mixed with *t*-BOC protected hexadecylamine (3.55 g, 0.0104 mol, 1.3 eq to allylic bromide) in a Haake Rheomix 600 batch mixer equipped with Banbury blades at 60 rpm and 50 ^{o}C for 10 min. Aliquots of the resulting masterbatch (5 g) were charged to an Advanced Polymer Analyzer (Alpha Technologies) operating with 3 degrees of arc at a frequency of 1 Hz.

2.5 References

[1] Parent, J.S., Thom, D.J., White, G., Whitney, R.A., and Hopkins, W.; Thermal Stability of Brominated Poly(isobutylene-*co*-isoprene). *Journal of Polymer Science Part A: Polymer Chemistry*, **39**, 2019-2026 (2001).

[2] Parent, J.S., White, G.D.F., and Whitney, R.A.; Amine Substitution Reactions of Brominated Poly(isobutylene-*co*-isoprene): New Chemical Modification and Cure Chemistry. *Macromolecules,* **35**, 3374-3379 (2002).

[3] Jorgensen E.; Reactions Between Carbon Dioxide and Amino Alcohols. *Acta Chemica Scandinavica*, **10**, 747-755 (1956).

[4] McGhee, W., Riley, D., Christ, K., Pan, Y., and Parnas, B.; Carbon Dioxide as a Phosgene Replacement: Synthesis and Mechanistic Studies of Urethanes from Amines, CO_2, and Alkyl Chlorides. *Journal of Organic Chemistry*, **60**, 2820-2830 (1995).

[5] George, M., and Weiss, R.G.; Chemically Reversible Organogels via Latent Gelators. Aliphatic Amines with Carbon Dioxide and Their Ammonium Carbamates. *Langmuir*, **18**, 7124-7135 (2002).

[6] Holas, T., Zbytovska, J., Vavrova, K., Berka, P., Madlova, M., Klimentova, J., and Hrabalek, A.; Thermotropic phase behavior of long-chain alkylammonium carbamates. *Thermochimica Acta*, **441**, 116-123 (2006).

[7] Strother, T., Hamers, R.J.,and Smith, L.M.; Covalent Attachment of Oligodeoxyribonucleotides to Amine-Modified Si (001) Surfaces. *Nucleic Acids Research*, **28**, 3535-3541 (2000).

[8] Brown B.R.; Amidines. From *The Organic Chemistry of Aliphatic Nitrogen Compounds*, 428-430, Rowlinson, J.S., Ed.; Oxford University Press, New York, 1994.

[9] Whitney, R.A., Penciu, A, Parent, J.S., Resendes, R, and Hopkins, W.; Cross-Linking of Brominated Poly(isobutylene-*co*-isoprene) by N-Alkylation of the Amidine Bases DBU and DBN. *Macromolecules*, **38**, 4625-4629 (2005).

[10] Shi, M., and Shen, Y.; A Novel Reaction of 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) or 1,5-Diazabicyclo[4.3.0]non-5-ene (DBN) with Benzyl Halides in the Presence of Water. *Helvetica Chimica Acta*, **85**, 1355-1363 (2002).

[11] Heldebrant, D.J., Jessop, P.G., Thomas, C.A., Eckert, C.A., and Liotta, C.L.; The Reaction of 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) with Carbon Dioxide. *Journal of Organic Chemistry*, **70**, 5335-5338 (2005).

[12] Perez, E.R., Santos, R.H.A., Gambardella, M.T.P., de Macedo, L.G.M., Rodrigues-Filho, U.P., Launay, J., and Franco, D.W.; Activation of Carbon Dioxide by Bicyclic Amidines. *Journal of Organic Chemistry*, **69**, 8005-8011 (2004).

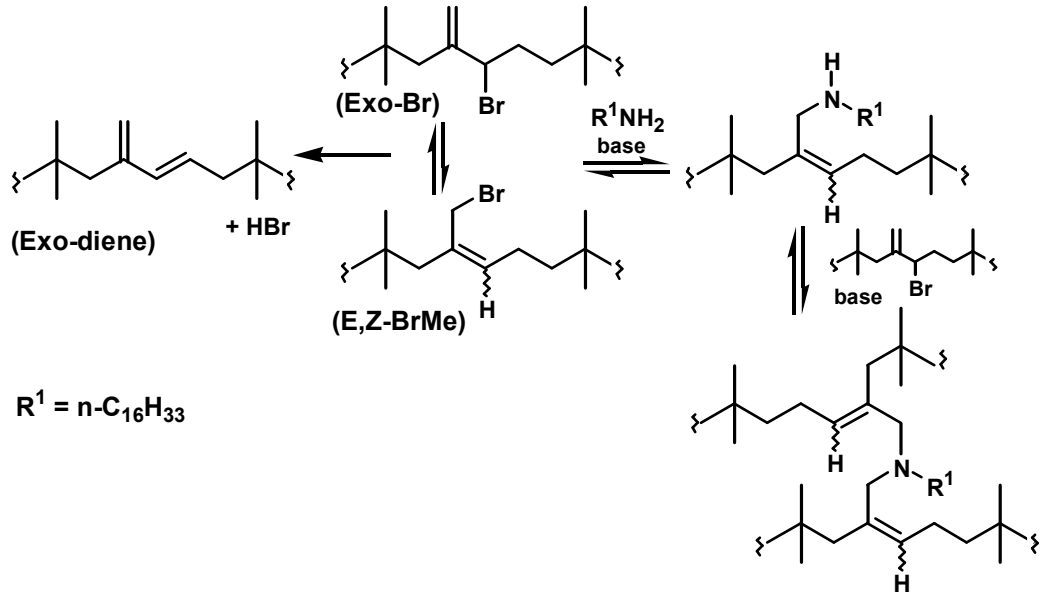
[13] Endo, T., Nagai, D., Monma, T., Yamaguchi, H., and Ochiai, B.; A Novel Construction of a Reversible Fixation-Release System of Carbon Dioxide by Amidines and their Polymers. *Macromolecules*, **37**, 2007-2009 (2004).

Chapter 3: Reactions of N-alkyl Benzaldimines with BIIR

3.1 Introduction

Random copolymers containing isobutylene and 1-2% isoprene (IIR) are elastomers that are valued for their impermeability to gases[1] and their stability with respect to oxidative degradation.[2] Bromination of poly(isobutylene-co-isoprene) yields BIIR,[3] whose susceptibility to allylic halide displacement by sulfur provides an efficient means of generating thermoset products.[4] BIIR cross-linking can also be accomplished by compounding with ZnO to initiate a complex series of cationic oligomerization reactions.[5,6] Both of these technologies are in widespread commercial use.

Scheme 3.1 N-Alkylation of BIIR with Primary Amine



Parent et al. have recently described alternate chemistry for cross-linking BIIR, wherein repeated N-alkylation of primary amines[7] and cyclic amidine bases[8] yields a covalent polymer network. The mechanism developed from rheological and model compound

studies of primary amine reactions is summarized in Scheme 3.1. The predominant isomer within BIIR is an exomethylene allyic bromide (Exo-Br), which rearranges upon heating to generate thermodynamically more stable E,Z-BrMe isomers. Temperatures on the order of 120°C also promote dehydrohalogenation to give an exo-methylene conjugated diene (Exo-diene). If not neutralized efficiently, the HBr eliminated by this process catalyzes subsequent isomerization, chain-scission, and cross-linking reactions that are generally undesirable. Therefore, commercial grades of BIIR typically contain $Ca(stearate)_2$ and/or epoxides to stabilize against secondary degradation reactions.

Primary amines do not accelerate HBr elimination from BIIR, but displace bromide to give mono- and bis-N-alkylation products. Since only the latter serve as polymer cross-links, the development of an amine-based cure formulation requires careful consideration of nucleophile concentration. Previous studies indicated an optimum of about 1.1 molar equivalents of primary amine relative to allylic bromide functionality. At this amine loading, sufficient nucleophile/base is present to drive the series of reversible bromide displacements toward the bis-N-alkylation product, and to make nucleophilic substitution rates competitive with dehydrobromination.

Given the wide array of available primary amines, this technology can yield thermosets that contain additional chemical reactivity. For example, a cure system based on $(MeO)_3SiCH_2CH_2CH_2NH_2$ may be attractive for BIIR composites that contain siliceous fillers. Unfortunately, amine alkylation is too fast at the temperatures that develop during rubber compounding. Therefore, the practicality of this chemistry would be improved by

techniques for controlling nucleophile delivery such that standard mixing operations can be used without scorch concerns. This has led us to examine latent forms of N-based nucleophiles that are easily handled, and can be activated by moisture and/or heat when desired. Whereas the dynamics of simple bromide displacements typically follow bimolecular substitution kinetics, a latent nucleophile can provide additional degrees of freedom to tailor reaction dynamics.

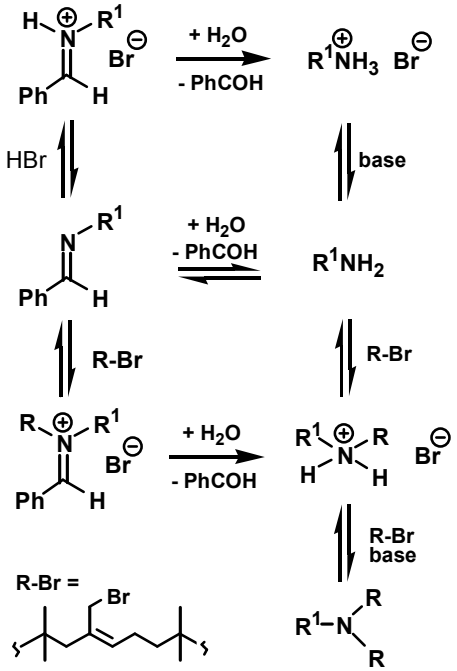
A simple method for rendering a primary amine as latent is through treatment with a carbonyl compound to form an imine (Schiff base). For this study, an aryl aldehyde, specifically benzaldehyde, was used as a source of carbonyl. Benzaldimines were chosen due to their ease of formation; aromatic aldehydes are known to react readily and quantitatively with amine.[9] Previous studies have determined that the resulting imines of this type exist in the *trans* configuration due to steric interactions of the R-groups of the parent aldehyde and amine,[9,10,11] with no phototropic isomerization to *cis* configuration.[12] This is due to the unavailability of an enolization pathway through photochromic conversion, as can be the case with aniline-derived benzaldimines.[13]

This chapter describes a variation of the Decker-Forster reaction – a selective method of generating secondary amines by N-alkylation of an imine with an alkyl halide, followed by hydrolysis of the resulting iminium ion.[14] This reaction sequence is designed to produce secondary amines while avoiding the bis-alkylation products that support a BIIR cure. This variation of the Decker-Forster reaction is designed to delay the onset of BIIR cross-linking by introducing a hydrolysis step to the cure process. If imine hydrolysis is

controlled adequately, the formulation will be inactive during compounding, but highly reactive at standard cure temperatures.

Scheme 3.2 illustrates several pathways for activating a N-alkyl benzaldimine for the purpose of BIIR cross-linking. Direct hydrolysis to give primary amine and benzaldehyde is the most straightforward process for imine activation. Ideally, this reaction would be slow at BIIR compounding temperatures (≈ 100°C), but capable of releasing amine quickly under curing conditions (≈ 160°C). The importance of a second activation pathway, N-alkylation followed by iminium ion hydrolysis, is dependent on the imine's nucleophilicity toward allylic bromide. If this pathway is to support a latent BIIR cure, imine alkylation must be slow at 100°C and/or the iminium ion must resist hydrolysis at this mixing temperature.

Scheme 3.2 Reaction Pathways of N-alkyl benzaldimine for BIIR Crosslinking



The significance of a third imine activation pathway depends on the rate of BIIR dehydrohalogenation. If temperatures are sufficient to promote HBr elimination, then the elastomer may support imine hydrolysis by generating a Bronsted acid catalyst *in situ*. If this pathway is to support a latent N-alkylation process, dehydrobromination must be negligible at 100°C, and only fast enough at 160°C to produce catalytic amounts of HBr. Extensive dehydrohalogenation is undesirable, since it decreases the amount of electrophile available for cross-linking.

This work sought to assess the utility of imines as delayed-onset curatives for BIIR, to identify the reactions that control the rate and yields of these cures, and to quantify the influence of electron donating and withdrawing substitutents on these reactions. To this end, a series of comprehensive rheological and model compound experiments for 1-hexadecylamine and its benzaldimine derivative is presented before examining the effect of para-subsitutents on cure performance.

3.2 Results and Discussion

3.2.1 N-alkyl Benzaldimines

Hexadecylamine ($C_{16}H_{33}NH_2$) is a solid (m.p. 45°C) that can be mixed with BIIR in conventional polymer processing equipment at 50°C. However, if temperatures reach 100°C, BIIR cross-linking is extensive, as illustrated by the dynamic rheological data plotted in Figure 3.1. These data were acquired using a BIIR compound containing 6.5 wt% of amine, which amounts to 1.3 molar equivalents of nucleophile relative to the 0.15 mmole of allylic bromide functionality per gram of starting material. Note that the

storage modulus (G') of this mixture increased from 74 kPa to 147 kPa within 20 min at 100°C. Subsequent heating to 160°C softened the material initially, but then accelerated the cure toward a plateau of 296 kPa.

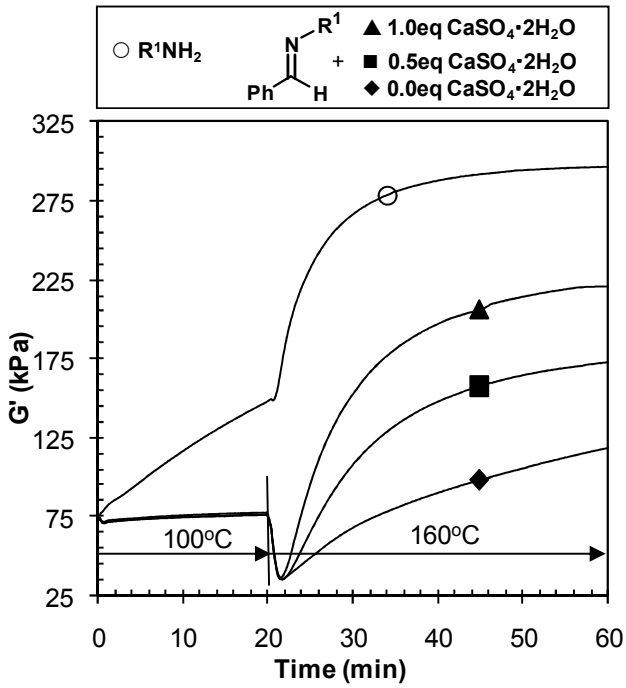


Figure 3.1 Storage modulus (G') of BIIR + 1.3 eq $C_{16}H_{33}NH_2$ and $PhCHNR^1$ formulations containing varying amounts of gypsum.

The same amount of N-hexadecylbenzaldimine ($PhCHNR^1$) produced very different BIIR cure dynamics (Figure 3.1). The storage modulus of this $PhCHNR^1$ formulation was virtually unchanged over 20 min at 100°C. Subsequent heating to 160°C generated a modest rate of cure that reached 117 kPa within 40 min. This relatively poor cure performance was due, in part, to inadequate moisture within the compound, which can be rectified by adding hydrated inorganic salts such as $CaSO_4 \cdot 2H_2O$. The data plotted in Figure 3.1 show that one equivalent of gypsum relative to imine raised the final modulus by a factor of 1.8 to a value of 220 kPa. This vulcanizate was extracted with chloroform,

and the supernatant was subjected to ^{1}H-NMR analysis to reveal an imine conversion to benzaldehyde of just 67%. This in part explains the low modulus of the PhCHNR[1] system relative to $C_{16}H_{33}NH_2$. Techniques for closing the performance gap between imines and free amines will be described following a brief examination of various imine activation pathways.

Scheme 3.2 illustrates three of the routes through which an imine can be activated to yield a BIIR vulcanizate. These include uncatalyzed imine hydrolysis, HBr-catalyzed hydrolysis, and N-alkylation followed by hydrolysis of the resulting iminium ion. Of these three pathways, direct imine hydrolysis can be ignored without introducing significant error to the analysis. This conclusion is based on independent hydrolysis experiments conducted in IIR and in dodecane solution. An IIR compound containing 0.26 mmole/g of PhCHNR[1] and 1 eq. of gypsum within the rheometer cavity produced no change in modulus over 6 hours at 160°C and, more importantly, resulted in no conversion of the imine to benzaldehyde. Similarly, maintaining a 0.075 M solution of N-hexadecyl benzaldimine at 160°C in the presence of 1 eq of gypsum converted just 3% of the reagent to benzaldehyde over a 1 hour period, and over 24 hours was required to consume all the starting material. Given the timescale of the studied BIIR cures, this unassisted hydrolysis process cannot deliver the amount of hexadecylamine that is needed to generate a modulus of 220 kPa.

N-alkylations of cyclic imines has been previously studied,[15] however the N-alkylation+iminium ion hydrolysis pathway appears to be insignificant for the PhCHNR[1]

system. Prolonged refluxing of a toluene solution containing PhCHNR[1] and brominated 2,2,4,8,8-pentamethyl-4-nonene (BPMN), a model compound for the allylic bromide functionality within BIIR, produced no observable changes. Apparently, this imine is not sufficiently nucleophilic toward the allylic halide functionality of interest. However, the inactivity of PhCHNR[1] is not universal, as electron donating substituents can improve the nucleophilicity of aryl imines substantially.[9] This will be demonstrated in the following section.

The potency of a third imine activation mechanism, Bronsted acid catalyzed hydrolysis,[16,17] was tested in a range of experiments. The most revealing experiment involved exposing a dodecane solution containing 0.075 M PhCHNR[1] to 0.2 eq HBr at 25°C. ^{1}H-NMR analysis of the mixture after 60 min revealed a 40% conversion of imine to benzaldehyde. Not surprisingly, hydrolysis was extensive when this solution was maintained for less than a minute at 160°C. This extreme sensitivity suggests that imine activation by this pathway can be dominant, and that BIIR dehydrohalogenation (Scheme 3.1) could play an important role. It was found that heating BIIR alone at 160°C converted 19% of allylic bromide to conjugated diene within 10 min, and 43% was converted after 20 min. In most BIIR derivatization reactions, dehydrobromination is undesirable, as it reduces the electrophile concentration available for polymer functionalization. Paradoxically, HBr elimination activates an imine cure while impacting negatively on cross-link yields.

Note that amine alkylation generates primary and secondary ammonium bromide salts that may also serve as sources of HBr (Scheme 3.1). The conjugate acid of an N-alkyl benzaldimine has a pK_A of about 13, compared with approx. 11 for an alkyl amine, meaning that imine protonation is favoured thermodynamically. This suggests that the alkylation reactions that give rise to BIIR cross-linking also support acid-catalyzed imine hydrolysis.

Therefore, water alone is insufficient to activate an imine formulation, and the latency of these cures is a product of controlled HBr release through dehydrohalogenation and/or N-alkylation + proton transfer. The demonstrated sensitivity of imines to acid-catalyzed hydrolysis would suggest that $PhCHNR^1$ conversions would be quantitative, yet only 67% of the imine was activated. This limited conversion has obvious implications for ultimate cure yields, and its origin lies not only with the volatility of HBr, but also with the acid scavengers added during BIIR manufacturing to mitigate HBr-catalyzed polymer degradation. In the present context, additives such as $Ca(stearate)_2$ and epoxidized soybean oil sequester HBr irreversibly, and limit the lifetime of the imine hydrolysis catalyst.

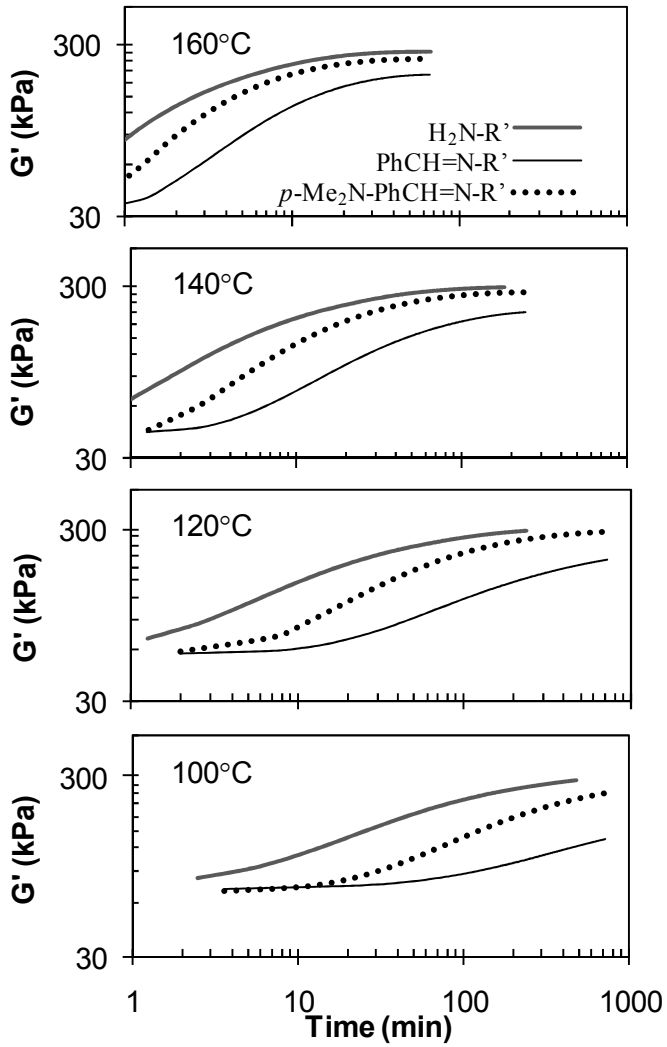


Figure 3.2 Double log plot of the storage modulus (G') versus time for BIIR + 1.3 eq amine/imine + 1.3 eq $CaSO_4 \cdot 2H_2O$ formulations at different temperatures.

The rheological data plotted in Figure 3.2 provide further insight into the dynamics of imine-based cures. The $C_{16}H_{33}NH_2$ reference data show evidence of curing from the onset of compound heating, with cure rates increasing in the early stages as mono-alkylation products progress to bis-alkylated amine cross-links. This progression is sufficiently rapid above 120°C that prolonged induction periods are not observed, but an early acceleration phase is observed at lower temperatures. In contrast, PhCHNR[1] cures

exhibit extended induction periods ranging from 2 min at 160°C to 40 min at 100°C, during which very little cross-linking takes place. These periods of inactivity are followed by pronounced acceleration phases where PhCHNR[1] cross-linking rates approach the highest values recorded for the $C_{16}H_{33}NH_2$ system.

Figure 3.3 shows the evolution of storage modulus and imine conversion for the 120°C cure generated by PhCHNR[1]. Note that imine hydrolysis progressed continuously from the earliest stages of the cure, with little response from G' in the first 10 min. This suggests that prolonged induction periods are the result of low active nucleophile concentrations. With little nucleophile present to drive the kinetics and equilibrium positions of N-alkylation, there is comparatively little crosslinking. As the extent of PhCHNR[1] activation increases, the modulus responds in turn.

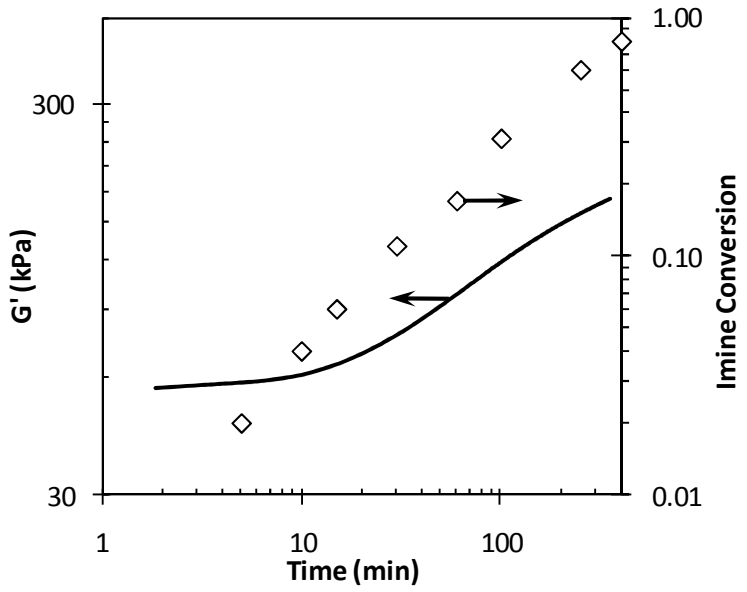


Figure 3.3 Log-log plot of storage modulus and PhCHNR[1] conversion versus time for BIIR + 1.3 eq imine + 1.3 eq $CaSO_4 \cdot 2H_2O$ at 120°C.

The data plotted in Figure 3.3 show that imine conversion at 120°C was incomplete, even though a significant amount of HBr must have been released through dehydrobromination and/or N-alkylation. This limited conversion has obvious implications for ultimate cure yields, and its origin lies not only with the volatility of HBr, but also with the acid scavengers added during BIIR manufacturing to mitigate HBr-catalyzed polymer degradation. In the present context, additives such as $Ca(stearate)_2$ and epoxidized soybean oil sequester HBr irreversibly, and limit the lifetime of the imine hydrolysis catalyst.

3.2.2 Imine Substituent Effects

The ultimate cross-linking yields generated by $PhCHNR^1$ are considerably lower. This difference reflects the cure efficiency loss that is suffered when the latent nucleophile is not activated rapidly. For an imine formulation to perform as well as a free amine, imine activation must be quantitative, and it must proceed faster than dehydrohalogenation, since the latter reduces the concentration of allylic bromide available for cross-linking.

If an imine formulation is to match the cross-link density generated by a primary amine, then its activation should not be solely dependent on HBr availability. It is noted above that $PhCHNR^1$ does not react significantly with the allylic bromide functionality within BIIR. However, its *p*–NMe_2 substituted analogue did react with the model compound, BPMN, in deuterated toluene at 100°C. Formation of an iminium salt will enhance the electrophilicity of the compound, favouring an increase in nucleophilic attack.[18] Clearly,

an electron-donating substituent acting on the imine nitrogen through conjugation improves its nucleophilicity, thereby increasing the importance of an N-alkylation+hydrolysis pathway for imine activation (Scheme 3.2). The rheology data presented in Figure 3.4 show that a *p*–NMe_2-PhCHNR^1 formulation generated a final storage modulus of 281 kPa - just 16 kPa lower than that generated by the free amine.

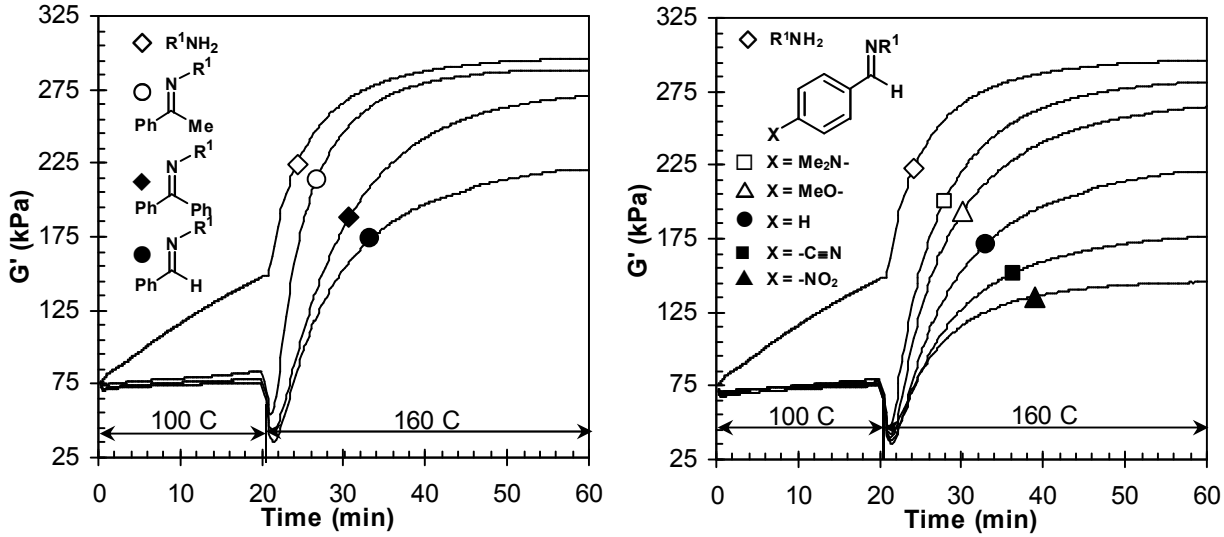


Figure 3.4 Substituent effects on BIIR cure dynamics and yields (T=160°C, 1.3 eq imine; 1.3 eq $CaSO_4 \cdot 2H_2O$).

The trends observed for other para-substituents were consistent with expectations, with cure efficiencies following the same order as the Hammett parameters, σ: Me_2N > MeO > H > CN > NO_2. Hammett parameters serve to demonstrate the theoretical free-energy relationship between the rate and equilibrium constant of a given reaction, specifically ionization. By examining the effect that a given substituent will have, an understanding on the possible reactivity of that compound can be inferred.[19] In this case, electron-rich substituents, such as Me_2N and MeO, have negative σ-values, meaning the ionization

tends to proceed much more regularly. This is due to these substituents providing electron density to the imine bond, favouring ion formation and increasing nucleophilicity. Methyl and phenyl substituents on the imine carbon generated similar effects, with the acetophenone-derived imine reaching the same modulus as $C_{16}H_{33}NH_2$ in an isothermal 160°C cure (Table 3.1). The electron-withdrawing substituents have positive σ –values, tending away from ion formation, decreasing nucleophilicity. Note that all of the imines studied exhibited prolonged latency periods at 100°C.

Table 3.1 Isothermal BIIR cure yields[a]

p-X-PhCRN-R'		Hammett Parameter[b]	pKa[c]	G' max	Imine
R	X	(σ)	(H_2O)	(kPa)	Conversion (%)
$C_{16}H_{33}NH_2$		---	≈11	294	---
1 -Me	---	---		294	100
2 -Ph	---	---		276	100
3 -H	-NMe_2	-0.44	16.9	288	100
4 -H	-OMe	-0.12	14.8	269	85
-H	---	---	13.3	220	67
5 -H	-CN	0.69		186	46
6 -H	-NO_2	0.82	11.0	146	42

a. 1.3 eq nucleophile; 160°C isothermal cures.

b. from source Taft Jr., R.W. J Phys Chem, 1960[20]

c. from source Minkin et al., CAN 70:67459[21]

The basicity of the imine relative to $C_{16}H_{33}NH_2$ and its BIIR-alkylated derivatives is also of interest, since the more basic the imine in comparison to the other bases in the mixture, the greater its hydrolysis rate. Subsitutent effects are well documented for *para*-substituted N-amylbenzaldimines, *p*-$RC_6H_4CH{=}NC_5H_{11}$, and the pK_A data and isothermal

cure yields provided in Table 3.1 reveal a close correlation. Increasing electron density not only affects nucleophilicity, but also the imine's basicity.

3.2.3 Electrophile Effects

Brominated poly(isobutylene-co-para-methylstyrene), or BIMS, is a specialty polymer containing on the order of 0.21 mmole of benzylic bromide functionality per gram of elastomer. Like BIIR, it is susceptible to halide displacement by nitrogen nucleophiles, as illustrated in Figure 3.5 for a BIMS mixture containing 1.3 molar equivalents of $C_{16}H_{33}NH_2$ relative to benzylic bromide. This formulation was more reactive than BIIR at 100°C, as evidenced by an 174 kPa increase in storage modulus in 20 min. Subsequent heating to 160°C raised the storage modulus to a final value of 476 kPa after 40 min. This is 180 kPa greater than observed for an equivalent BIIR formulation (Figure 3.1). Allowing for the higher initial modulus of BIMS, it is still clear that the benzylic bromide provides a higher state of an amine cure than does the allylic bromide within BIIR. This is likely due to differences in the propensity of the two polymers to undergo dehydrobromination, as well as differences in the thermal stability ammonium intermediates.

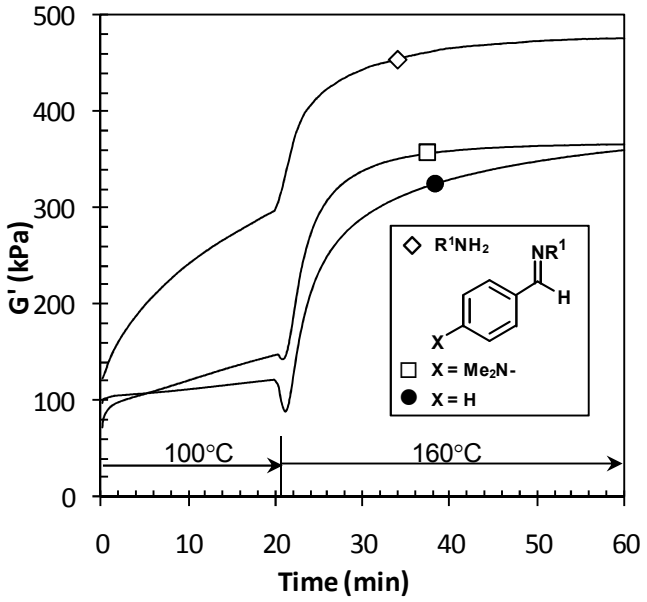


Figure 3.5 Storage modulus (G') of BIMS + 1.3 eq $C_{16}H_{33}NH_2$ and X-PhCHNR[1] formulations (1.3 eq imine; 1.3 eq $CaSO_4 \cdot 2H_2O$).

Notwithstanding the observed reactivity of BIMS, PhCHNR[1] can provide delayed onset cure characteristics for this electrophile. The data plotted in Figure 3.5 show a slight increase in modulus over 20 min at 100°C, likely resulting from slow N-alkylation of the imine by benzylic bromide. This was not observed for the allylic bromide system, which was inactive with respect to PhCHNR[1] in both model compound studies and BIIR cure experiments. Recall, however, that *p*-NMe_2-PhCHNR[1] does react with the allylic bromide of interest, thereby providing an additional pathway to activate electron-rich benzaldimines. In the case of BIMS formulations, electron donating groups such as –NMe_2 increase imine nucleophilicity to the extent that substantial cure reactivity is observed even at 100°C, thereby compromising the desired delayed-onset characteristics.

3.3 Conclusions.

Reactions between primary amines and allylic bromides cross-link BIIR at conventional processing temperatures, necessitating the use of latent sources of this nucleophile. Uncatalyzed imine hydrolysis is too slow to compete with allylic bromide dehydrohalogenation, even in the presence of excess moisture. However, acid-catalyzed hydrolysis provides effective imine activation pathways, owing to the HBr eliminated directly by BIIR, and made available by the ammonium bromide products of N-alkylation. The need for moisture and HBr for N-hexadecyl benzaldimine activation underlies the extended induction periods observed by cure rheology. Imines bearing electron-donating substituents are sufficiently nucleophilic to react directly with allylic bromide functionality, yielding an allyl iminium ion that is highly susceptible to hydrolysis. As a result, this class of latent imine curatives are more efficient than electron-deficient analogues.

3.4 Experimental.

Materials. BPMN was prepared as described previously.[22] 1-Hexadecylamine (technical grade, 90%), benzaldehyde (≥ 99%), acetophenone (99%), benzophenone (≥ 99%), 4-methoxybenzaldehyde (98%), 4-(dimethylamino)benzaldehyde (99%), 4-cyanobenzaldehyde (95%), 4-nitrobenzaldehyde (98%), HBr (48 wt% in H_2O, 99.999%), dodecane (anhydrous, ≥ 99%) and calcium sulfate dihydrate (gypsum, 98%) were used as received from Sigma Aldrich (Oakville, Ont.). BIIR (LANXESS BB2030, $M_w \approx 400{,}000$, allylic bromide content ≈ 0.20 mmol/g) was used as supplied by LANXESS Inc. (Sarnia,

Ont.). BIMS (EXXPRO 3745, benzylic bromide content ≈ 0.21 mmol/g) was used as supplied by Exxon Mobil Chemical.

Synthesis of N-hexadecyl benzaldimine. Benzaldehyde (1.68 g, 0.016 mol) was added drop-wise to 1-hexadecylamine (3.28 g, 0.014 mol) and heated to 110°C in a Kugelrohr distillation apparatus (17 mmHg) for 5 hours, yielding a yellow-brown liquid. The imine was used without further purification. No residual amine was evident by NMR analysis. ^{1}H NMR ($CDCl_3$): δ (ppm) = 8.27 (1H, s, RN=C**H**Ph), 7.73 (2H, m, arom), 7.40 (3H, m, arom.), 3.61 (2H, t, =N-CH_2-), 1.71 (2H, m, CH_2), 1.32 (26H, m, -CH_2-), 0.90 (3H, t, -CH_3).

Synthesis of *para*-substituted N-hexadecyl benzaldimines. 1-Hexadecylamine was charged to a round-bottom flask and mixed with a slight molar excess of the desired *p*-substituted benzaldehyde, acetophenone, or benzophenone. The resulting solutions were heated to 115^{o}C in a Kugelrohr distillation apparatus (17 mmHg) for 6 hours.

1 N-hexadecyl methylphenylketimine: (500 MHz, CDCl3): ^{1}H δ (ppm) = 7.76 (2 H, m, arom.), 7.36 (3 H, m, arom.), 3.47 (2 H, t, =N-CH_2-), 2.23 (3 H, s, =N-CH_3), 1.26 (29 H, m, -CH_2-), 0.88 (3 H, t, -CH_3).

2 N-hexadecyl diphenylketimine: (500 MHz, CDCl3): ^{1}H δ (ppm) = 7.8-7.1 (multiplets, arom.), 3.39 (2 H, t, =N-CH_2), 1.28 (29 H, m, -CH_2-), 0.90 (3 H, t, -CH_3).

3 N-hexadecyl *p*-dimethylaminobenzaldimine: (500 MHz, CDCl3): ^{1}H δ (ppm) = 8.15 (1 H, s, N=C-H), 7.60 (2 H, m, arom.), 6.71 (2 H, m, arom.), 3.55 (2 H, t, =N-CH_2-), 3.03 (6 H, s, Ph-N-$(CH_3)_2$), 1.27 (29 H, m, -CH_2-), 0.90 (3 H, t, -CH_3).

4 N-hexadecyl *p*-methoxybenzaldimine: (500 MHz, CDCl3): ^{1}H δ (ppm) = 8.19 (1 H, s, N=C-H), 7.66 (2 H, m, arom.), 6.93 (2 H, m, arom.), 3.84 (3 H, s, O-CH_3), 3.56 (2 H, t, =N-CH_2-), 1.25 (29 H, m, -CH_2-), 0.88 (3 H, t, -CH_3).

5 N-hexadecyl *p*-cyanobenzaldimine: (500 MHz, CDCl3): ^{1}H δ (ppm) = 8.29 (1 H, s, N=C-H), 7.82 (2 H, m, arom.), 7.69 (2 H, m, arom.), 3.64 (2 H, t, N-CH_2-), 1.25 (29 H, m, -CH_2-), 0.88 (3 H, t, -CH_3).

6 N-hexadecyl *p*-nitrobenzaldimine: (500 MHz, CDCl3): ^{1}H δ (ppm) = 8.34 (1 H, s, N=C-H), 8.25 (2 H, m, arom.), 7.87 (2 H, m, arom.), 3.65 (2 H, t, =N-CH_2-), 1.23 (29 H, m, -CH_2-), 0.86 (3 H, t, -CH_3).

BIIR cure reactions with amine. BIIR (40 g) was mixed with hexadecylamine (2.60 g, 1.3 eq to allylic bromide) in a Haake Rheomix 600 batch mixing bowl equipped with Banbury blades at 60 rpm and 50^{o}C for 10 min. Aliquots of the resulting masterbatch (5 g) were charged to an Advanced Polymer Analyzer (Alpha Technologies) operating with 3 degrees of arc at a frequency of 1 Hz.

BIIR cure reactions with imine. BIIR (40 g) was mixed with a N-hexadecyl benzaldimine or ketimine (1.3 eq to allylic bromide) and calcium sulfate dihydrate (gypsum, 1.92 g, 1.3 eq to allylic bromide) in a Haake Rheomix 600 batch mixer equipped with Banbury blades at 60 rpm and 50 ^{o}C for 10 min. Aliquots of the resulting masterbatch (5 g) were charged to an Advanced Polymer Analyzer (Alpha Technologies) operating with 3 degrees of arc at a frequency of 1 Hz.

3.5 References

[1] Boyd, R.H., and Pant, P.V.K.; Molecular Packing and Diffusion in Polyisobutylene. *Macromolecules*, **24**, 6325-6331 (1991).

[2] Dubey, V., Pandey, S.K., and Rao, N.B.S.N.; Review Research Trends in the Degradation of Butyl Rubber. *Journal of Analytical and Applied Pyrolysis*, **34**, 111-125 (1995).

[3] Vukov, R.; Halogenation of Butyl Rubber – A Model Compound Approach. *Rubber Chemistry and Technology*, **57**, 284-290 (1984).

[4] Parent, J.S., White, G.D.F., Thom, D., Whitney, R.A., and Hopkins, W.; Sulfuration and Reversion Reactions of Brominated Poly(isobutylene-co-isoprene), *Journal of Polymer Science, Part A: Polymer Chemistry*, **41**, 1915-1926 (2003).

[5] Vukov, R.; Zinc Oxide Crosslinking Chemistry of Halobutyl Elastomers - A Model Compound Approach. *Rubber Chemistry and Technology,* **57**, 284-290 (1984).

[6] Hendrikse, K. G., and McGill, W. J.; Vulcanization of Chlorobutyl Rubber. II. A Revised Cationic Mechanism of ZnO/ $ZnCl_2$ Initiated Crosslinking. *Journal of Applied Polymer Science*, **78**, 2302-2310 (2000).

[7] Parent, J.S., White, G.D.F., and Whitney, R.A.; Amine Substitution Reactions of Brominated Poly(isobutylene-*co*-isoprene): New Chemical Modification and Cure Chemistry. *Macromolecules,* **35**, 3374-3379 (2002).

[8] Whitney, R.A., Penciu, A, Parent, J.S., Resendes, R, and Hopkins, W.; Cross-Linking of Brominated Poly(isobutylene-*co*-isoprene) by N-Alkylation of the Amidine Bases DBU and DBN. *Macromolecules*, **38**, 4625-4629 (2005).

[9] Layer, R.W.; The Chemistry of Imines. *Chemical Reviews*, **63**, 489-510 (1963). and references therein.

[10] Karabatsos, G.J, and Fenoglio, D.J.; Rotation Isomerism About *sp2-sp3* Bonds: IV. Imino Compounds. From *Topics in Stereochemistry*, Vol. 5, Eliel, E.L., and Allinger, N.C., Eds.; J. Wiley and Sons, New York, 1970.

[11] Curtin, D.Y., and Hausser, J.W.; Effects of Structural Changes on the Interconversion of Stereoisomeric Imines. Isoelectronic Models for Vinyl Anions. *Journal of the American Chemical Society*, **83**, 3474-3481 (1961).

[12] De Gaouck, V., and Le Fevre, R.J.W.; Stereochemistry of Anils. *Journal of the Chemical Society*, 741-745 (1938).

[13] McCarty, C.G.; syn-anti Isomerizations and Rearrangements. From *The Chemistry of the Carbon-Nitrogen Double Bond*, 363-464, Patai, S., Ed.; J. Wiley and Sons, Toronto, 1970.

[14] Decker, H., and Becker, P.; Quaternary Salts of Alkylideneamines and a General Method for the Alkylation of Primary to Secondary Amines. *Justus Liebigs Annalen der Chemie*, **395**, 362-377 (1913).

[15] Nomura, Y., Bando, T., Takeuchi, Y., and Tomoda, S.; Novel N-Alkylation of a Schiff Base with Electron-Deficient Olefins. *Tetrahedron Letters*, **36**, 3453-3456 (1979).

[16] Cordes, E.H., and Jencks, W.P.; On the Mechanism of Schiff Base Formation and Hydrolysis. *Journal of the American Chemical* Society, **84**, 832-837 (1962).

[17] Barra, M., Croll, L.M., Tan, A., and Tao, W.; Kinetic Studies on the Proton-Catalysed Hydrolytic Decomposition of Quinone-Imine Dyes. *Dyes and Pigments*, **53**, 137-142 (2002).

[18] Brown, B.R.; Iminium Salts. From *The Organic Chemistry of Aliphatic Nitrogen Compounds*, 161-167, Rowlinson, J.S., Ed.; Oxford University Press, New York, 1994.

[19] Hammett, L.P.; *Physical Organic Chemistry*, 2nd Edition, 347-390, McGraw-Hill, New York, 1970.

[20] Taft, R.W.; Sigma Values from Reactivities. *Journal of Physical Chemistry*, **64**, 1805-1815 (1960).

[21] Minkin, V.I., Bren, V.A., and Malysheva, E.N.; Basicity and Structure of Azomethines and their Structural Analogues. III. Analysis of the Substituent Electron Effect in Benzalkylimine Nucleus on their Basicity by Correlation Analysis and Quantum Chemistry. *Reaktsionnaya Sposobnost Organicheskikh Soedinenii*, **5**, 565-582 (1968). CAN 70:67459.

[22] Parent, J.S., Thom, D.J., White, G., Whitney, R.A., and Hopkins, W.; Thermal Stability of Brominated Poly(isobutylene-*co*-isoprene). *Journal of Polymer Science Part A: Polymer Chemistry*, **39**, 2019-2026 (2001).

Chapter 4: Influence of Amines and Imines on Conventional BIIR Cure Formulations

4.1 Introduction

This chapter describes the influence of nitrogen-based nucleophiles on conventional BIIR cure formulations. In these cases, sulfur and/or ZnO chemistry is designed to generate the requisite cross-link density, while a relatively small amount of a functional amine provides additional chemical reactivity. One example would be $(MeO)_3SiCH_2CH_2CH_2NH_2$ to promote phase adhesion in silica-filled composites. To be effective in such an application, the amine must react with BIIR without complicating the compound mixing process or impacting negatively on the cross-link density of the cured article.

The effect of 1-hexadecylamine and N-hexadecyl benzaldimine on was examined for three curative systems: sulfur-only, ZnO-only, and sulfur+ZnO. Whereas sulfur-only formulations are of purely academic interest, ZnO-only cures are used in pharmaceutical stoppers, and sulfur+ZnO cures are commonplace in tire inner liner applications. The objective of this study was to quantify the extent to which relatively small amounts of N-nucleophile affected the stability of these formulations at 100 °C, and their cure reactivity at 160°C.

4.2 Results and Discussion

4.2.1 Conventional Cure Dynamics

Before investigating the effect of nitrogen nucleophiles on conventional cures, it is important to determine baseline cure performance in the absence of such additives. Figure 4.1 illustrates the crosslink dynamics provided by three BIIR cure formulations: sulfur-only, ZnO-only, and sulfur+ZnO. The sulfur-only system provided a maximum G' of 238 kPa, but cure reversion was extensive as the modulus declined continuously beyond the 20 min mark of the vulcanization process. This behavior is well established for BIIR cures, and it prevents the use of sulfur-only formulation in commercial rubber goods manufacturing.

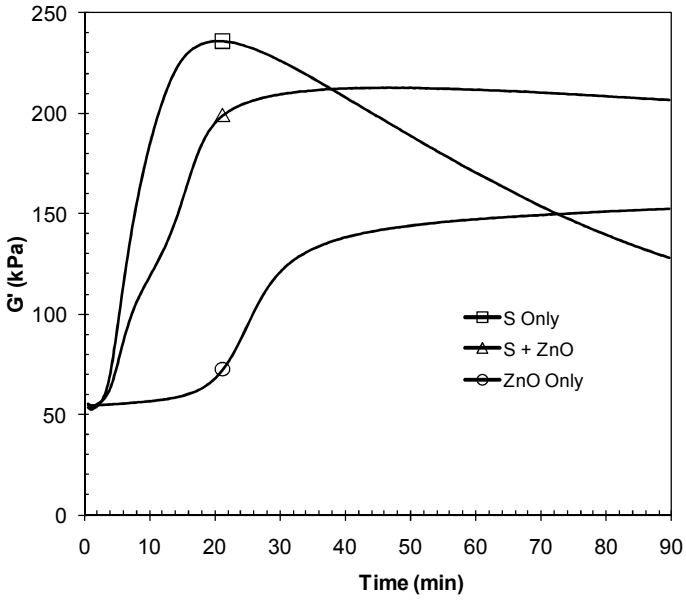


Figure 4.1 Cure comparisons of S-alone, ZnO-alone, and S + ZnO at 160 ^{o}C

The ZnO-only crosslinking dynamics shown in Figure 4.1 are consistent with other reports, in that a pronounced induction period was followed by a moderate cure. Unlike its sulfur-only counterpart, the ZnO cure does not suffer from reversion, but shows a tendency toward sustained cross-linking, a phenomenon known as "marching modulus". As described in Chapter 1, the chemistry underlying ZnO cures is not well understood. However, the observed induction period is commonly attributed to the need to generate Lewis acid derivatives of ZnO *in situ* by the release of HBr from the polymer. The resulting acidic Zn species are, presumably, capable of catalyzing a cationic oligomerization of residual C=C functionality within the polymer.

The crosslinking dynamics generated by the sulfur+ZnO system are particularly interesting, owing to an apparent "double cure" (Figure 4.1). The initial cure may be the result of sulfuration, while the second a result of zinc oxide activation. Note that BIIR dehydrobromination is believed to activate zinc oxide in a ZnO-only formulation, but the generation of persulfenyl bromide byproducts in a sulfur+ZnO formulation may accelerate this activation process. Further study is required to define the interaction of ZnO and these reactive RS_nBr intermediates, but it is reasonable to assume that they are responsible for the apparent shortening of the ZnO cure induction period.

4.2.2 Influence of Amines and Imines on Conventional Cures

Figure 4.2 illustrates the cross-linking activity of BIIR that was compounded with 0.25 eq of 1-hexadecylamine and heated to 100 ^{o}C for 20 min, followed by 40 min at 160 ^{o}C. This compound cured at 100 ^{o}C to a storage modulus of 128 kPa - an increase of 30 kPa

from its initial value. This extent of crosslinking is too great for industrial applications, as the material would be cured before it could be processed in a mold.

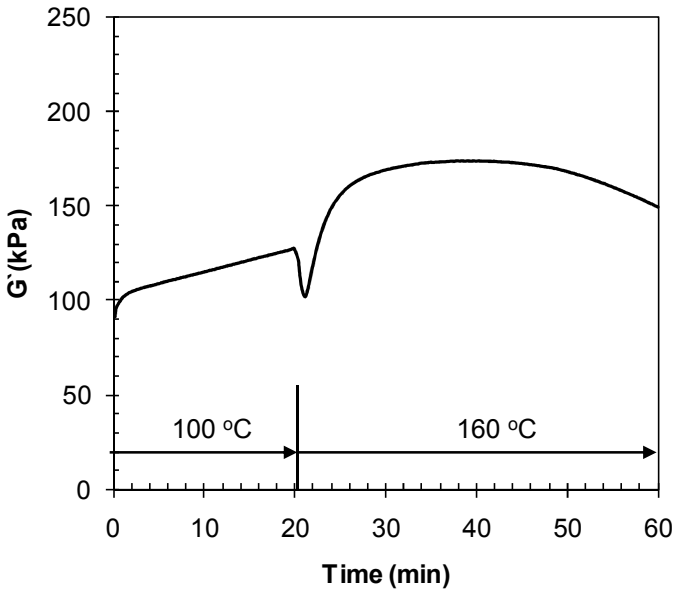


Figure 4.2 Storage modulus of BIIR + 0.25 eq $C_{16}H_{33}NH_2$, 100°C/160°C

Given the effect that 0.25 eq of 1-hexadecylamine had on BIIR alone, the cure activity of sulfur and ZnO formulations containing the free amine is not surprising (Figure 4.3). In contrast, 0.25 eq of N-hexadecyl benzaldimine, PhCHNR[1], did not induce low temperature scorch problems for either the cure system. In fact, the modulus of the imine-containing compounds was lower than the rest of the compounds due to the plasticizing effect of a soluble small molecule on BIIR. Further benefits were realized for both cure formulations, as the imine raised the ultimate modulus of the sulfur only system, and reduced the induction period that is observed for ZnO only formulations.

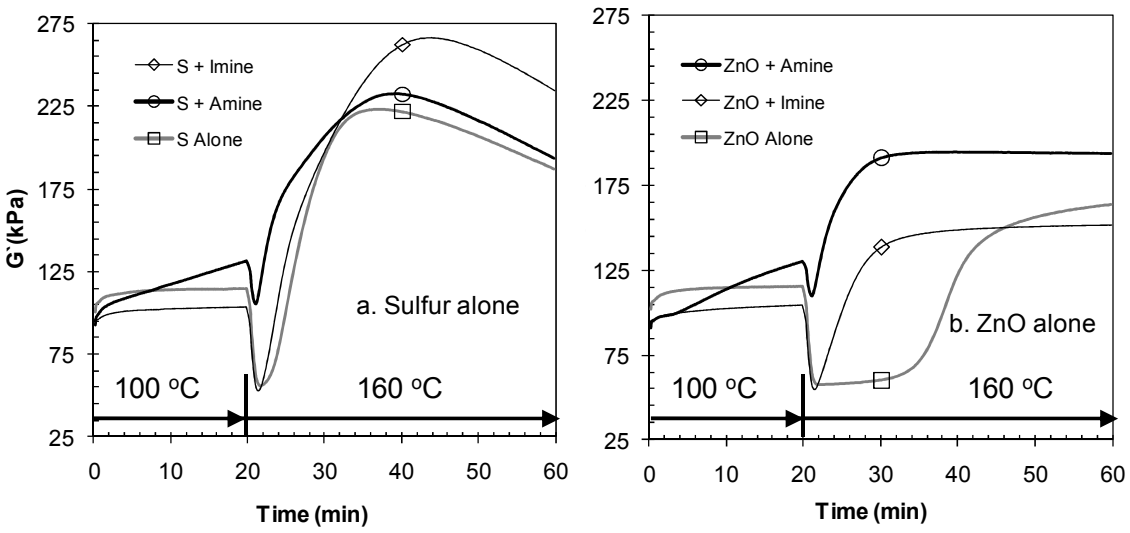


Figure 4.3: BIIR cure dynamics (0.25 eq nucleophile; 1.5 phr S or 3.0 phr ZnO)

Figure 4.4 illustrates the effect of hexadecylamine and N-hexadecyl benzaldimine on sulfur+ZnO cure formulations. While the amine cures the compound significantly at 100 °C, the imine serves only to plasticize the compound at this temperature. Both additives accelerated the onset of the cure at 160 °C, more so than with sulfur being the only nucleophilic species available (See Figure 4.1). Also of note is the absence of a "double cure" feature in formulations containing amine and imine. This may be due to an increased availability of HBr, arising from halide displacement from allylic bromide by the additional nucleophile. The subsequent activation of zinc allows for that pathway to become available much sooner in the curing process.

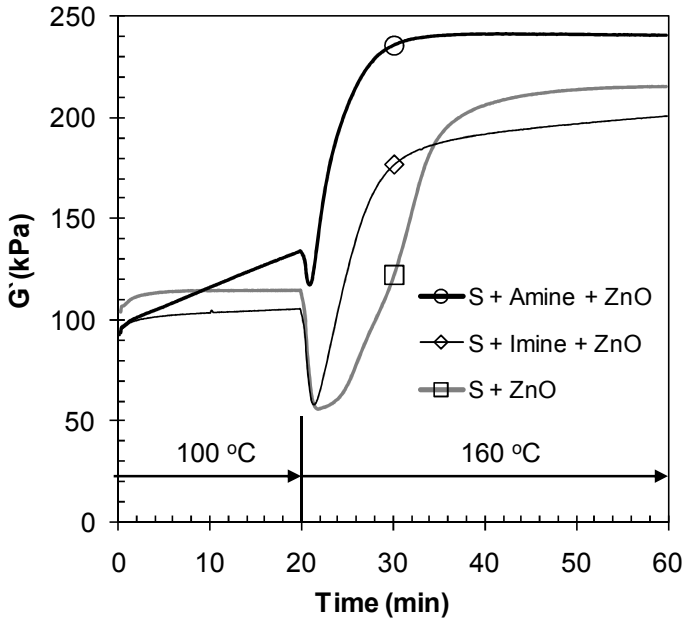


Figure 4.4 BIIR cure dynamics with S + ZnO (0.25 eq nucleophile, 100°C/160°C)

The ability of amines and imines to activate a ZnO cure is remarkable. Consider the data plotted in Figure 4.5, in which only 0.03 eq of $C_{16}H_{33}NH_2$ or PhNCHR[1] were added to a 3.0 phr ZnO cure formulation. This small amount of N-based nucleophile cannot support an N-alkylation cure, and all samples were stable at 100 °C. Surprisingly, the amine and imine containing compounds cured rapidly upon heating to 160 °C, with scorch delays of less than 2-3 min. Neither nucleophile affected the overall cure extent. In terms of industrial significance, the ability to accelerate the onset of a cure that normally has a 20 minute induction period without having an effect on the end product has the potential to improve the efficiency and output of such a process.

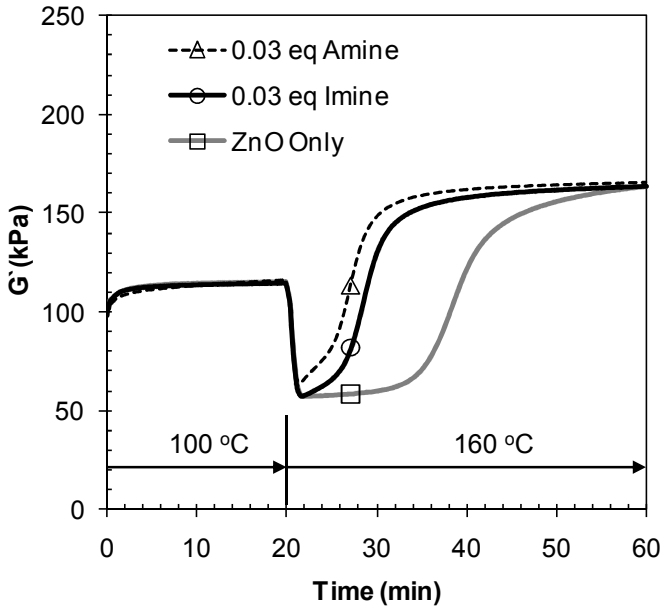


Figure 4.5 BIIR cure dynamics with 3.0 phr ZnO + 0.03 eq nucleophile, 100°C/160°C

4.3 Conclusions

When compounded into BIIR in significant quantities, primary amines give rise to excessive crosslinking rates at 100 °C, thereby precluding their use as additives in conventional cure formulations. However, N-alkyl benzaldimine analogues create no such scorch problems, thereby providing a means of using functional amines in conventional BIIR compounding processes. When used in very small quantities, both imines and amines are potent activators for ZnO-only cure systems, eliminating the induction period normally observed for these industrial processes.

4.4 Experimental

Materials. BIIR (LANXESS BB2030, $M_n \approx 400{,}000$, allylic bromide content ≈ 0.20 mmol/g), sulfur, and zinc oxide (Kadox 920) were used as supplied by LANXESS Inc. (Sarnia, Ont.). 1-Hexadecylamine (technical grade, 90%) and benzaldehyde (≥ 99%) were used as received from Sigma Aldrich (Oakville, Ont.).

Synthesis of N-hexadecyl benzaldimine. Benzaldehyde (1.68 g, 0.016 mol) was added drop-wise to 1-hexadecylamine (3.28 g, 0.014 mol) and heated to 110°C in a Kugelrohr distillation apparatus (17 mmHg) for 5 hours, yielding a yellow-brown liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.27 (1H, s, RN=C**H**Ph), 7.73 (2H, m, arom), 7.40 (3H, m, arom.), 3.61 (2H, t, =N-CH_2-), 1.71 (2H, m, CH_2), 1.32 (26H, m, -CH_2-), 0.90 (3H, t, -CH_3).

Vulcanization of BIIR with Sulfur. BIIR (40 g) was mixed with sulfur (0.21 g, 0.5 phr or 0.62 g, 1.5 phr) in a Haake Rheomix 600 batch mixer equipped with Banbury blades at 60 rpm and 50 ^{o}C for 10 min. Aliquots of the resulting masterbatch (5 g) were charged to an Advanced Polymer Analyzer (Alpha Technologies) operating with 3 degrees of arc at a frequency of 1 Hz.

Vulcanization of BIIR with Sulfur and Zinc Oxide. BIIR (40 g) was mixed with sulfur (0.62 g, 1.5 phr) and ZnO (1.21 g, 3 phr) in a Haake Rheomix 600 batch mixer equipped with Banbury blades at 60 rpm and 50°C for 10 min. Aliquots of the resulting

masterbatch (5 g) were charged to an Advanced Polymer Analyzer (Alpha Technologies) operating with 3 degrees of arc at a frequency of 1 Hz.

Vulcanization of BIIR with Zinc Oxide. BIIR (40 g) was mixed with ZnO (1.21 g, 3 phr) in a Haake Rheomix 600 batch mixer equipped with Banbury blades at 60 rpm and 50 ^{o}C for 10 min. Aliquots of the resulting masterbatch (5 g) were charged to an Advanced Polymer Analyzer (Alpha Technologies) operating with 3 degrees of arc at a frequency of 1 Hz.

Influence of Primary Amine on Sulfur Cure Acceleration. BIIR (40 g) was mixed with sulfur (0.62 g, 1.5 phr) and 1-Hexadecylamine (0.65 g, 0.25 eq to allylic bromide) in a Haake Rheomix 600 batch mixer equipped with Banbury blades at 60 rpm and 50 ^{o}C for 10 min. Aliquots of the resulting masterbatch (5 g) were charged to an Advanced Polymer Analyzer (Alpha Technologies) operating with 3 degrees of arc at a frequency of 1 Hz.

Influence of Primary Amine on Sulfur-Zinc Oxide Cure Acceleration. BIIR (40 g) was mixed with sulfur (0.62 g, 1.5 phr), ZnO (1.21 g, 3 phr), and 1-Hexadecylamine (0.65 g, 0.25 eq to allylic bromide) in a Haake Rheomix 600 batch mixer equipped with Banbury blades at 60 rpm and 50 ^{o}C for 10 min. Aliquots of the resulting masterbatch (5 g) were charged to an Advanced Polymer Analyzer (Alpha Technologies) operating with 3 degrees of arc at a frequency of 1 Hz.

Influence of Primary Amine on Zinc Oxide Cure Acceleration. BIIR (40 g) was mixed with ZnO (1.21 g, 3 phr) and 1-Hexadecylamine (0.65 g, 0.25 eq to allylic bromide) in a Haake Rheomix 600 batch mixer equipped with Banbury blades at 60 rpm and 50 ^{o}C for 10 min. Aliquots of the resulting masterbatch (5 g) were charged to an Advanced Polymer Analyzer (Alpha Technologies) operating with 3 degrees of arc at a frequency of 1 Hz.

Influence of N-hexadecyl benzaldimine on Zinc Oxide Cure Acceleration. BIIR (40 g) was mixed with ZnO (1.21 g, 3 phr) and N-hexadecyl benzaldimine (0.94 g, 0.25 eq to allylic bromide) in a Haake Rheomix 600 batch mixer equipped with Banbury blades at 60 rpm and 50 ^{o}C for 10 min. Aliquots of the resulting masterbatch (5 g) were charged to an Advanced Polymer Analyzer (Alpha Technologies) operating with 3 degrees of arc at a frequency of 1 Hz.

Influence of Catalytic N-hexadecyl benzaldimine on Zinc Oxide Cure Acceleration. BIIR (40 g) was mixed with ZnO (1.21 g, 3 phr) and N-hexadecyl benzaldimine (0.12 g, 0.03 eq to allylic bromide) in a Haake Rheomix 600 batch mixer equipped with Banbury blades at 60 rpm and 50 ^{o}C for 10 min. Aliquots of the resulting masterbatch (5 g) were charged to an Advanced Polymer Analyzer (Alpha Technologies) operating with 3 degrees of arc at a frequency of 1 Hz.

Influence of Catalytic Primary Amine on Zinc Oxide Cure Acceleration. BIIR (40 g) was mixed with ZnO (1.21 g, 3 phr) and 1-Hexadecylamine (0.079 g, 0.03 eq to allylic

bromide) in a Haake Rheomix 600 batch mixer equipped with Banbury blades at 60 rpm and 50 ^{o}C for 10 min. Aliquots of the resulting masterbatch (5 g) were charged to an Advanced Polymer Analyzer (Alpha Technologies) operating with 3 degrees of arc at a frequency of 1 Hz.

Chapter 5: Conclusions

5.1 CO_2-Derived Delayed Onset Nitrogen Nucleophiles

The reactivity of free amine makes BIIR cure formulations scorchy. By converting the free nucleophile into a CO_2-protected salt, latency can be introduced through thermal decomposition. 1.0 eq of ammonia, in the form of a CO_2 salt such as ammonium carbonate, cured BIIR at 160^{o}C to a final storage modulus of 220 kPa while showing scorch stability at 100 ^{o}C. TGA analysis revealed that the carbonate salt decomposes readily below 100 ^{o}C, meaning the scorch stability is a result of solubility and kinetic considerations of the N-alkylations required for curing.

A CO_2-derived carbamate salt of 1-hexadecylamine, $C_{16}H_{33}NH_2$, decomposed at 60 ^{o}C, resulting in inadequate scorch protection. Protecting the primary amine with a *t*-butyl carbamate ester significantly raised the decomposition temperature, however dehydrobromination reduced the amount of available electrophile once the nucleophile was liberated.

A bicarbonate salt of DBU exhibited relatively stable cure behaviour at 100^{o}C, but a high degree of activity at 160 ^{o}C. While achieving an extent of cure less than that of free DBU, the ability of the bicarbonate salt to supply its own water means no other additives are needed.

5.2 Reactions of N-alkyl Benzaldimines with BIIR

By chemically protecting a primary amine in the form of an imine, latency can be governed by hydrolysis rather than thermal decomposition. For an N-hexadecyl benzaldimine, uncatalyzed imine hydrolysis is too slow to compete with dehydrobromination. Even in the presence of excess moisture, the rate of hydrolysis is too slow to support an effective cure. In contrast, acid-catalyzed hydrolysis provides effective imine activation pathways, owing to the HBr eliminated directly by BIIR, and made available by the ammonium bromide products of N-alkylation. The need for moisture and HBr for N-hexadecyl benzaldimine activation underlies the extended induction periods observed by cure rheology.

Modifying the benzaldimine with electron-donating substituents, the observed cure extent was increased. The additional electron density renders the imine sufficiently nucleophilic to react directly with allylic bromide functionality, yielding an allyl iminium ion that is highly susceptible to hydrolysis. Imines with electron-withdrawing substituents had the reverse effect. As a result, this class of latent imine curative is less efficient.

5.3 Influence of Amines and Imines on Conventional BIIR Cure Formulations

When compounded into BIIR in significant quantities, primary amines give rise to excessive crosslinking rates at 100 °C, making them unsuitable for industrial use.

However, N-alkyl benzaldimine analogues create no such scorch problems, thereby providing a means of using functional amines in conventional BIIR compounding.
In order to be an effective cure accelerator, the compound must provide reactivity without negatively affecting the crosslink chemistry of sulfur and/or ZnO. Amine (0.25 eq) added to a conventional cure formulation resulted in a moderate 30 kPa increase in storage modulus at lower temperature. An equivalent amount of imine did not exhibit this scorch behaviour, as the imine is not nucleophilic enough to significantly cure BIIR at this loading. Neither nucleophile had a negative impact on the overall state of cure.

In ZnO cures, the presence of a nucleophilic species accelerated the onset of the cure, indicating that the activation of ZnO is sensitive to the presence of HBr in the system. Even in small amounts, a nucleophilic species can substantially accelerate a ZnO cure.

5.4 Future Work

Additional investigation into the scope of imine alkylation chemistry would be beneficial. A substituted N-alkyl benzaldimine is an effective delayed-onset curative, however upon hydrolysis a small-molecule is eliminated. This may pose concerns in an industrial application. A cyclic imine analogue such as an oxazoline would simply ring-open upon hydrolysis, yet remain bound to the polymer backbone. DBU demonstrates this behaviour, however the free nucleophile is too reactive with BIIR.

Additional experiments with regard to the performance of the curatives with polymers such as chlorobutyl rubber (CIIR) and BIMS would be of interest. The change in electrophile could result in development of additional applications where one cannot exist with BIIR.

Given the performance of imine as a conventional cure accelerator, additional work should be undertaken to determine the feasibility of using it as a modifier for functional additives. As a previously stated example, a cure system based on aminopropyltriethoxysilane, $(MeO)_3SiCH_2CH_2CH_2NH_2$, would be a compatibilizer for silica-based fillers. Protection of the amino group would allow for controlled delayed-onset reaction, the result being a functionalized BIIR composite.