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Spectroscopic studies of accelerated-sulfur vulcanized cis-polyisoprene

Krejsa, Michael Robert, Ph.D.
Case Western Reserve University, 1992
SPECTROSCOPIC STUDIES OF ACCELERATED–SULFUR
VULCANIZED CIS–POLYISOPRENE

by

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Submitted in partial fulfillment of the requirements
for the Degree of Doctor of Philosophy

Dissertation Advisor:
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January, 1993
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GRADUATE STUDIES

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SPECTROSCOPIC STUDIES OF ACCELERATED—SULFUR VULCANIZED CIS-POLYISOPRENE

Abstract

by

MICHAEL ROBERT KREJSA

Solid-state C-13 NMR and H-1 NMR spin-spin (T2) relaxation measurements were used to probe the network structure of accelerated sulfur vulcanized cis-polyisoprene. Two different accelerator systems were analyzed: tert-butyl benzothiazole sulfenamide (TBBS) and tert-butyl benzothiazole sulfenimide (TBSI). Network structures in both accelerators were similar, and consisted solely of allylic substitution, with limited double bond migration. Most sulfurization products were polysulfidic, though moderate amounts of monosulfidic products were observed. The network structures were correlated with accelerator derivatives measured in HPLC measurements, and key cure and maturation reactions elucidated. Spin-spin (T2) measurements were used to determine the effect of crosslink and cyclic structures on the relaxation behavior.
DEDICATION

This work is dedicated to my wife Regina for her patience, understanding, and encouragement shown me during my graduate career. I would also like to dedicate this to our two cats, Charlie and Tony.
ACKNOWLEDGEMENTS

The author wishes to thank Professor Jack L. Koenig for his support, guidance and motivation in the course of this work. Sincere thanks are also extended to the Macromolecular Spectroscopy Group, both present and graduated, for their valuable suggestions and guidance.

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CHAPTER I

A REVIEW OF THE PRESENT UNDERSTANDING OF THE FUNDAMENTAL SCIENCE OF UNACCELERATED AND ACCELERATED SULFUR VULCANIZATION OF RUBBER
I. INTRODUCTION

Elastomers are one of the oldest and widely used polymers known to man, which accounts for their use in a variety of applications. Originally natural rubber was used uncured, but suffered from drastic softening in warm weather and highly increased rigidity in cold weather [1]. The first significant elastomeric technology advancement was the simultaneous discovery in England and the United States that addition of sulfur to rubber, followed by heating, leads to an improvement in the properties. This was the first vulcanization system, and was discovered by Goodyear in the U.S. and Hancock in England [1].

Pure sulfur vulcanization, while alleviating many of the disadvantages of pure elastomers, does not provide an optimum product. Around 1910 it was discovered by Oeslänger in Germany that the addition of aniline to a rubber/sulfur formulation greatly increased the rate of vulcanization and improved the final vulcanizate properties [1]. It was quickly discovered that a wide variety of amines functioned similarly. These amines were the first accelerators for vulcanization.
Presently there are a wide range of accelerator systems available for elastomers, providing a range of cure rates, scorch times and final properties. These accelerators include the thiurams, sulfenamides, sulphenimides, mercaptobenzothiazoles, amines; several common accelerators are shown in Table I [2]. Additionally, there are combination systems (i.e., thiuram sulfenamides) also available. The variety of accelerators accounts for the wide applicability of elastomers to material applications. Also of increasing utility are binary accelerator systems, which utilize two or more accelerators in a synergistic manner. Mixed in the proper proportions, binary systems can lead to significant improvement in curing behavior and mechanical properties.

In addition to sulfur and sulfur/accelerator vulcanization systems, elastomers can be crosslinked by a variety of other techniques including radical initiators (peroxides), irradiation, ultraviolet and metal oxide cures. This article will review the literature and state of knowledge for the pure sulfur and accelerated sulfur vulcanization systems, but will not discuss other techniques for crosslinking rubber. The first half of this review will cover unaccelerated sulfur vulcanization, while the second half will
elucidate the current knowledge of accelerated sulfur formulations. This review article will summarize work performed in the rubber field since 1962. For an excellent and very complete review of work on the fundamental science of vulcanization prior to 1962, the reader should consult Chapter 15 of "The Chemistry and Physics of Rubberlike Substances" [3].

The importance of understanding the network structures of cured elastomers can be seen from Tables II through IV [4] and Figure 1 [5]. These tables detail empirical relationships between degree and type of crosslink and/or sulfurization structures and end-use properties. Ideally, rubber formulators would like to choose rubber formulations based on the desired end properties. Presently, this is done based on past experience and results. The ultimate goal of understanding vulcanization chemistry is to be able to tailor formulations to produce desired mechanical and chemical properties. If we can develop a full understanding of the relationship between vulcanization chemistry and the resulting network then this goal can be obtained.
There are two general categories of sulfur vulcanization: unaccelerated and accelerated sulfur. Unaccelerated sulfur formulations consist of rubber and sulfur, while accelerated sulfur systems contain rubber, accelerator and sulfur. In addition, zinc oxide and stearic acid are often included in both types of systems. There are also accelerator systems in which elemental sulfur is not present; instead, the accelerator provides the sulfur for vulcanization. These systems are referred to as sulfurless, or sulfur-donor, systems.

A typical cure rheometer trace is shown in Figure 2 [6]. This graph illustrates the three main regions of cure (labeled I–III). The first region is the scorch delay period or induction period, in which the majority of the accelerator chemistry takes place. The second period is the cure period, in which the initial network structures are formed and the accelerator intermediates are consumed. The final stage is the overcure, or reversion period, during which network maturation and resulting property deterioration occurs.

An overall scheme of vulcanization is shown in Figure 3 summarizing the key steps of the accelerated sulfur vulcanization reactions. The formation of the accelerator complex and active sulfurating species will
be discussed in one section, and the formation and aging of the vulcanizate network will be discussed in another section. Emphasis will be placed on the analytical techniques or methods used to study the vulcanization process, and the specific knowledge gained from each methodology. Additionally, the network structures will be discussed in detail, and their relationship to vulcanization chemistry detailed whenever possible.
II. UNACCELERATED SULFUR VULCANIZATION

Vulcanization with pure sulfur, also referred to as unaccelerated sulfur vulcanization, is the oldest vulcanization formulation, and as such has been widely studied. While unaccelerated sulfur vulcanization is not widely used today, a large number of works evaluating the chemistry and network structures of this type of system has been performed. The inherent simplicity of pure sulfur vulcanization precludes the necessity of understanding the precise nature of accelerator behavior and interactions.

With the simplicity of pure sulfur formulations, one would expect more easily understood behavior then for accelerated sulfur systems. However, the reverse is actually true. The vast array of work in this area has found that pure sulfur chemistry enhances many reactions that either do not occur or occur to much lesser extents in accelerated systems. These reactions range from double bond migration, isomerization and saturation to chain cleavage, cyclization and formation of vicinal crosslinks [3,7-13].
Most knowledge of pure sulfur vulcanization has been derived from model compound work, and subsequent analysis of these materials. The original research in this area was performed in the late 1950's and early 1960's, and focused heavily on the work performed in the Natural Rubber Producers Research Association (NRPPRA), now MRPRA (Malaysian Rubber Producers Research Association) [3]. A major focus of the unaccelerated sulfur vulcanization has been the nature of the reaction mechanism. Significant discussion has revolved around the issue of polar (ionic), radical or mixed mechanisms for vulcanization. To answer this question, several techniques including radical scavengers [14] and EPR analysis [15] have been used. Additionally, the specific network structures detected in vulcanizates and model compounds have been used to argue for or against certain mechanistic schemes.

Shelton and McDonel [14] used radical scavengers to evaluate vulcanization mechanisms. From their studies they concluded that unaccelerated sulfur vulcanization is a polar process. Another approach, which was used by Blokh [15], was the use of electron paramagnetic resonance (EPR) studies. Based on the absence of a radical signal in the EPR studies Blokh concluded that unaccelerated sulfur vulcanization
proceeds via a polar mechanism.

A major cause of the disagreement on the mechanism of unaccelerated sulfur vulcanization arises from the possible reactions of sulfur. The $S_2$ ring is capable of undergoing homolytic (radical) and heterolytic (polar/ionic) ring opening reactions.

The proposed mechanism for free radical sulfurization postulates formation of sulfur radicals via homolytic scission of the octet sulfur ring as illustrated in Figure 4 [3]. The sulfur radical abstracts a proton from the rubber to form an elastomer radical. The elastomer radical then ring-opens the sulfur ring to form a rubber-bound sulfur radical capable of forming crosslink structures. Alkyl-alkyl products and vicinal crosslinks are formed if the crosslinked rubber radical added sulfur instead of abstracting a proton. Isomerization and double bond migration is accounted for in Figure 5 [3]. The rubber radical exists in two allylic structures. Sulfur addition to the radical can occur in either structure; if sulfur addition occurs at the quaternary carbon then double bond migration results. Cis-trans isomerization results from the formation of the rubber radical, followed subsequently by reformation of the rubber unit without sulfur addition. This mechanistic scheme has
the advantage of accounting for alkenyl-alkyl products and double bond migration (Figure 4), and cis-trans isomerization (Figure 5).

The proposed polar mechanism for unaccelerated sulfur vulcanization is shown in Figures 6 and 7 [3]. Figure 6 illustrates the mechanism for proton transfer, while Figure 7 is a more generalized version allowing for either proton or hydride transfer. The key step is the formation of the three-membered sulfur-carbon charged ring. For this mechanism isomerization occurs through the nonsulfurated rubber ion; when this ion reforms the elastomeric repeat unit, the olefinic moiety can reform in either the cis or trans configuration. This reaction mechanism also explains the formation of alkenyl-alkyl structures. Alkyl-alkyl structures result from the saturated persulfenyl rubber ion reacting with a rubber molecule, followed by proton transfer. The formation of cyclic structures is shown in Figure 8 [3]. The sulfur crosslink can cleave at the relatively labile S-S bond; the sulfur chain then reacts intramolecularly to form a cyclic structure.

Related to the formation of cyclic structures is the reduction of rank of crosslinks with increasing cure time. There are several proposed reaction schemes; the mechanism that is commonly favored is an
exchange reaction between the crosslink and the
sulfurating intermediates. This reaction terminates
upon formation of monosulfidic structures.

Several approaches have been used to analyze the
network structures resulting from unaccelerated sulfur
vulcanization. One approach has been the use of model
compounds. This has been used for both
model compounds used in these experiments are shown in
Figure 9. These model compound studies have detected
network structures consisting primarily of
alkenyl-alkyl structures (Figure 10) or cyclic
structures with double bond migration (Figure 10)
[3,11]. More recently solid-state C-13 NMR has been
used to directly measure the network structure
[8-10,13]. These studies detected the sulfurization
structures shown in Figure 11, which are similar to
those in predicted by model compound studies (Figure
10). Specifically, alkenyl-alkyl structures, cyclic
structures, and cis-trans isomerization were observed.
The one significant difference between the NMR and
model compound studies is that the NMR studies measured
larger amounts of alkenyl structures than the model
compound work predicted.
Kruger and McGill have performed DSC analysis of the interactions of sulfur with ZnO stearic acid [16]. Their results indicated the formation of zinc stearate, and also found that the zinc stearate reacted with the sulfur, changing its thermal transitions. The sulfur-zinc stearate interaction helps to explain the activating role of zinc oxide in unaccelerated sulfur vulcanization, but does not detail the actual interactions. Further work is needed to fully elucidate the specific interactions between zinc stearate and sulfur.

The general conclusion to date is that unaccelerated sulfur vulcanization occurs via a polar reaction mechanism. Both the radical scavenger studies [14] and the EPR studies [15] point in this direction. Additionally, the free radical mechanism would be expected to result in much higher levels of double migration in natural rubber and cis-polyisoprene than is observed [3,9,10]. This expectation results from the fact that a radical mechanism would result in a quaternary radical in isoprene elastomers; the stability of this radical would favor double bond migration if reformation of the double bond occurs.
III. ACCELERATED SULFUR VULCANIZATION

Accelerated sulfur formulations are the most common vulcanization systems used in commercial and industrial applications, and because of this, there is a large body of ongoing work into both the fundamental and applied aspects of accelerated sulfur vulcanization. The majority of this research concentrates on single accelerator systems due to their widespread use and the fact that the chemistry of single accelerators systems is inherently simpler. However, the amount of research into the fundamental chemistry of binary accelerators systems is rapidly growing. The impetus for the increasing use of binary systems derives from several factors including a desire to optimize the end-use properties and better control of processing safety. This review will thus discuss single accelerator and binary systems separately.

A sub-category of accelerated sulfur vulcanization is the area of sulfurless systems. There are very few compounds of this nature, but the accelerator chemistry of these systems is very interesting, is applicable to sulfur-containing formulations, and these formulations are in industrial use.
The section on accelerated sulfur vulcanization will be divided into four areas. The first area is a review of the papers elucidating the behavior of the accelerator and accelerator intermediates. The second area will deal with the cure and network maturation (reversion) periods, in which the network is formed and then subsequently matures. Additionally, separate sections will review the work into sulfurless (sulfur-donor) systems, and binary accelerator systems.
A. ACCELERATED SULFUR SYSTEMS

1. SCORCH DELAY PERIOD

The scorch delay, or induction period (Region I, Figure 2) is when the majority of the accelerator chemistry occurs. It should be noted that the length of scorch delay varies widely between accelerators. There is little, if any, induction time in the thiuram accelerator systems. Mercaptobenzothiazole also has a very short induction time, while the amine derivatives of MBT, the sulfenamides and sulfenimides, are used in many applications because of their long scorch delays.

The general scheme for vulcanization shown in Figure 3 illustrates the key reactions during this time period. During the scorch delay, various accelerator complexes are formed. The literature on accelerator chemistry is replete with a variety of conclusions as to the exact nature and role of these complexes. While it is clear that specific complexes do form, whether or not these complexes are the actual sulfurating species, or whether an activated intermediate is formed is still open for debate.
It should be noted that the consensus to date is that the key accelerator species formed are of the nature:

\[
\begin{array}{c}
\text{Ligand} \\
\downarrow \\
\text{X} \cdots \text{S}_x \cdots \text{Zn} \cdots \text{S}_y \cdots \text{X} \\
\uparrow \\
\text{Ligand}
\end{array}
\]

Where \( \text{L} \) = ligand, such as amines, and \( \text{X} \) is the accelerator moiety, such as:

\[
\begin{array}{c}
\text{CH}_3 \quad \text{S} \\
\text{CH}_3 \quad \text{N} \quad \text{C}
\end{array}
\]

Several techniques have been used to study the induction period. One of the more widely used techniques for probing the chemistry during this time period has been Differential Scanning Calorimetry (DSC) [17-24]. DSC has proved to be a useful, if indirect, tool for understanding the relationships and interactions between the various curative components.

The most common application of DSC to analyze vulcanization chemistry has been to study the thermal interactions between all possible combinations of
curatives in a specific formulation. This approach has
been used by McGill and coworkers [17,19,20,22-24], and
also by Kok et. al. [23] and Luyt [21]. These
studies have yielded interesting insights into
accelerator interactions. Many of these studies have
studied MBT accelerated vulcanization [17,18,21], or
vulcanization with derivatives of MBT [18,21,23]. Zinc
was found to form zinc complexes with MBT but not with
MBTS [23,24]:

\[
\text{Zn} + \begin{array}{c}
\text{N} \\
\text{C} \\
\text{S} \\
\text{H}
\end{array} \rightarrow \begin{array}{c}
\text{N} \\
\text{C} \\
\text{S} \\
\text{Zn}
\end{array}
\]

\[
\text{Zn} + \begin{array}{c}
\text{N} \\
\text{C} \\
\text{S} \\
\text{Sx}
\end{array} - \begin{array}{c}
\text{N} \\
\text{C} \\
\text{S}
\end{array} \rightarrow \text{No Reaction}
\]

The zinc-MBT complex formation did not go to
completion, which Luyt [21] concluded slowed the
sulfurization reaction. Zinc did react with stearic
acid to form zinc stearate [21,23]. For TMTD systems,
DSC analysis detected no reaction of zinc with TMTD or
TMTM, which is a product of TMTD decomposition [19,20].
Kruger et.al proposed that TMTM and TMTD form TMTP
[19]:
The formation of TMTP was detected originally by Coleman et. al [25], which will be discussed in a later section. Kruger argued that the actual sulfurating species is TMTP, not ZnDMDC as others have proposed. Additionally, they argue that the role of zinc oxide is to catalyze the conversion of rubber-bound intermediates to crosslinks. These conclusions suggest that TMTD-accelerated vulcanization differs in a fundamental manner from benzothiazole-accelerated vulcanization, which is discussed in the following sections.

Another approach to understanding accelerator chemistry is to determine the distribution of accelerator complexes and other curatives as a function of cure time. This approach was used by Campbell and Wise [26,27] and Hann et.al. [28,29]. The work of Hann et.al. involved analysis of cis-polyisoprene vulcanized with tert-butyl benzothiazole sulfenamide [28] and tert-butyl benzothiazole sulfenimide [29], while the work of Campbell and Wise studied MBT, MBTS and MOR vulcanization of natural rubber both in the presence [27] and absence [26] of zinc oxide and stearic acid. The exact nature of these accelerators during the cure process is shown in Figures 12 [27] for MBT and in Figure 13 for TBSI [29]. These four works
provide some insight into general characteristics of the chemical behavior of benzothiazole-based accelerators. During the induction period the concentration of polythiobisbenzothiazole (Figure 12) reached a maximum shortly before the beginning of crosslinking as is shown in Figure 12 [27]. During the cure period MBT content increased, reaching a maximum at approximately full cure. Sulfur content was found to decrease, reaching zero at full cure. It should be noted that the measured MBT content consisted of MBT and ZnMBT. Campbell and Wise also analyzed the state of zinc during the vulcanization process. Their results, shown in Figure 13 [27], illustrate that the extractable zinc decreases as a function of cure time. This data coupled with the work of Coran [30], which detected the presence of the zinc complex BtSxZnSxBt (Figure 12) during the vulcanization process, suggests that the zinc complex BtSxZnSxBt is a key accelerator intermediate [30]. This has also been the conclusion of Krejsa et.al. in a combined NMR/HPLC analysis [31].

Indirect evidence as to the nature of the accelerator complex derives from a study involving isotopic labeling of the amine fragment of the sulfenamide accelerator [32]. In this study, Aarts et.al. determined via N-15 labeling and subsequent
analysis by N-15 solid-state NMR that the amine was not lost during the vulcanization process. They also concluded that it was still bonded to sulfur, but the exact nature of the sulfur-nitrogen interaction was not clear. This result suggests that the amine is present in the accelerator complex. The most probable form of this would be as a ligand of the type shown previously.

The argument over radical vs. polar mechanisms has raged through the rubber literature for nearly 40 years. A wide variety of techniques have been used to address this issue; these approaches have included radical scavenger studies [14,33-35], ESR analysis [15,25,36-38], the combined use of dicumyl peroxide and accelerators in the formulation [39-49], and analysis of a wide variety of accelerators [34]. The disagreement and wide range of conclusions derives from the mechanism of accelerated sulfur vulcanization in Figure 3 which was discussed in a previous section. The exact nature of the sulfurlating species and accelerator complexxes will determine the polar or radical nature of the reaction mechanism.

The use of flash photolysis has been one of the more novel techniques in this area [50]. While this work was primarily aimed at analyzing oxidation reactions, is used the thiazy radical:
The authors also looked at the reactivity of various elastomers to the presence of the thiazyl radical. Ito et al. found that the reactivity of the various elastomers to be very different as shown in Figure 14 [50]. This has important implications for vulcanization formulations, as it suggests that if different mechanisms are operative, the favored mechanism is a function of the elastomer present.

Radical scavenger studies have also been used to study this issue. Early work in this area was performed by Shelton and McDonel [14]. Their conclusions vary widely as a function of the accelerator formulation used. Duchacek used a modified version of this approach in his work [33,35] by including thiourea in his formulations. Thiourea is a known radical scavenger; this allowed Duchacek to analyze the radical/polar nature of the reaction mechanisms by analyzing the change in kinetics and extent of cure with the addition of thiourea. Morita and Young [34] used radical scavengers; they also included acid and base acceptors to fully elucidate the nature of the reaction mechanism. They concluded that sulfenamide accelerators contain mixed ionic and radical mechanisms. Additionally, they concluded that the scorch delay and vulcanization rate are a function
of the basicity and steric structure of the amine component of the accelerator, and of the accelerator/sulfur ratio. A summary of the conclusions of the radical scavenger papers as they apply to accelerated sulfur systems is shown in Table V.

The technique of Electron Spin Resonance (ESR) has also been used to study this question [15,25,36,38]. The original use of ESR to study vulcanization was by Blokh [15]. His work suffered from copper impurities in the zinc oxide [25], thus leading to questions about the validity of his work. Banerjee also used this technique to study sulfenamide vulcanization in the presence of carbon black [38], and n-cyclohexylthiophthalimide (CPT) [36]. CPT, which has the chemical formula:

![Chemical Structure of CPT]

is a widely used inhibitor for vulcanization due to its properties of increasing the scorch delay without affecting the extent of crosslinking. The conclusion of Banerjee was sulfenamide accelerated sulfur vulcanization is predominantly polar in nature. Coleman et. al. [25] studied TMTD-accelerated sulfur
vulcanization using ESR. They concluded that TMTD/S is ionic initially, but the crosslinking reaction is radical. This will be discussed in greater detail in the sulfurless cure section.

Banerjee and coworkers have studied a large number of systems through the addition of dicumyl peroxide (DCP) to the formulation [39-49]. This approach uses the high reactivity of the peroxide radicals to interfere with radical reactions of the accelerator complexes. If the vulcanization chemistry is ionic, then the radical reactions do not interfere, and no effect of addition of DCP is observed. The conclusions of these papers are listed in Table VI. The overall trend of this work is that TMTD tends to favor radical or mixed polar/radical reactions, while MBT or derivatives coupled with ZnO and stearic acid will favor mixed polar/radical or purely polar reactions. Zinc oxide in general will tend to favor polar or mixed polar/radical reactions.

Several authors have studied the effect of amines on vulcanization [51-55]. These studies have looked at several amines, but the most studied amine was hydrofuramide [52-54]. Hydrofuramide has been found to increase the percent cure, decrease the scorch time, and increase the vulcanization rate. Other amides give
similar results [51].

Bravar and coworkers used kinetic analysis to elucidate the role of hydrofuramide [55]. They found that the activation energy for vulcanization was dependent on both carbon black and hydrofuramide. This work illustrates the importance of all components of the accelerator formulation on the vulcanization chemistry. The amines help to stabilize complex formation, but components such as carbon black can preferentially adsorb amines, limiting the stabilizing power of these amines.

Other authors have studied the kinetics of vulcanization as an indirect means of analyzing the vulcanization chemistry. Duchacek analyzed the effect of fillers and temperature on the kinetic rate constants and activation energy of vulcanization [56,58,59]. His study into the effect of zinc oxide concentration lead to the conclusion that in a TMTD system, zinc oxide and TMTD form the compound ZnDMDC [56]. This was based in part on the fact that the optimum zinc/TMTD ratio was a mole ratio of approximately 1:1.
Duchacek also analyzed the effect of carbon black [58] and silica [59] on the kinetics of TMTD-accelerated vulcanization. His conclusions were that silica served to catalyze the formation of ZnDMDC. He based this on comparing the activation energy of a silica-filled system compared with TMTD/S and ZnDMDC accelerated vulcanization. Carbon black did not show similar results, however. Duchacek found that carbon black does change the value of the rate constant but does not change the measured activation energy, which he attributed to carbon black inducing secondary crosslinking.

Further support of the Duchacek's argument for formation of ZnDMDC is his comparison of the kinetics of TMTD/S formulations to ZnDMDC formulations [33]. The induction time decreased in the ZnDMDC systems, but the rate constant of vulcanization was similar.

Several papers have looked at the nature of the accelerator complexes via techniques other than those already discussed. Chatterjee and Sircar [60] measured the reaction of MBT with rubber during preparation of formulation. Their extractions of the uncured, mixed elastomers lead to the conclusion that a small percentage of MBT was attached to the rubber after mixing. Rakhman et. al. [61] analyzed the effect of
various metal oxides on the extent of cure. Their work concluded that a variety of metal oxides can accelerate cure, but the degree of acceleration varies with the specific metal ion used. Milligan studied the role of metal-accelerator-carboxylate (stearic acid) complexes in network formation [62]. His studies illustrated the importance of ligands in stabilizing the zinc salt (ZnMBT in his work). This agrees well with the amine work mentioned previously, as well as the much older practice of covulcanizing using DPG. Amines increase the activity of the complex [62], usually in conjunction with stearic acid (or similar fatty acids).

Several authors have looked at the chemistry of inhibition to better understand the chemistry of vulcanization [36,63–65]. Banerjee used ESR to analyze the role of the pre-vulcanization inhibitor [36] N-cyclohexylthiophthalimide (CPT) on the vulcanization chemistry. He concluded that the inhibition is due to the ionic reaction:

\[
\begin{align*}
\text{N-C-S}^- + \text{O-C-N-S-S-} & \rightarrow \text{O-C-N-}^- + \text{N-C-S-S-}
\end{align*}
\]
Ananad and coworkers also reached similar conclusions [65].

Loo and coworkers studied the formation of inhibitors in situ in formulations with high accelerator concentration [64]. They concluded that the inhibitors formed were of one of the two forms:

\[ R_2N-S-S-NR_2 \]

The formation of these inhibitors in situ is evidenced by the rheometer trace shown in Figure 15 [64], which illustrates a two-plateau behavior. The intermediate plateau derives the in situ formation of the inhibitors shown above.
2. CURE AND MATURATION REGIMES

The cure and maturation period of elastomers (Figure 2, Region III), has been studied by an array of analytical and chemical approaches. Model compound studies have been widely used [4, 66-71], as have kinetic studies [24, 33, 56-59, 72-74]. Chemical probe techniques, which cleave specific sulfur chain lengths, have been used to quantify the length of crosslink structures [3, 75]. Analytical techniques such as UV [32], Raman [25, 76-79], infrared [7, 80, 81], and C-13 NMR [8-10, 13, 31, 82-85, 87-89, 93, 94], are used to probe the vulcanized network during the cure and reversion processes. Recuring of fully cured vulcanizates has been used to probe the role of sulfur and accelerator during vulcanization and reversion [89, 90]. The changes in network structure during postcuring and reversion have also been studied [91].

The chemical probe technique is actually one of the older techniques in analysis of vulcanizates [3], with the original work dating into the 1950’s. A major advance in this area was the work of Cuneen and Russell [75]. Their work involved the application of several chemical probe formulations. The significant difference between these thiol-based chemical probes
and the older probes is the increased selectivity of the reagents used. Many works in the rubber literature now use chemical probe studies as an auxiliary technique in their research.

Model compound studies is one of the older techniques for analyzing accelerated sulfur vulcanization [3]. Interest in this approach has remained high, as it continues to show good agreement with actual vulcanizate structures. Gregg and Katrenick [69] used this approach for polybutadiene accelerated with MBTS and DPG. They determined that significant amounts of cyclization would occur, as would polysulfidic crosslinks and saturation of the double bond. The later work of Gregg and Lattimer [92] suggested that the model compound used for this study, cis,cis-1,5-cyclooctadiene, was not an accurate model for polybutadiene as at least three allylic double bonds are needed to model the reactivity of polybutadiene.

Skinner [70] analyzed the CBS-accelerated vulcanization of natural rubber and polybutadiene using model compound analysis and chemical probe studies. The model compound analysis suggested that allylic sulfurization would occur as is seen in Figure 16 [70]. These structures are primarily allylic substitute, with
small amounts of double bond migration and saturation. Figures 17 and 18 [70] illustrate the sulfur rank for the cis-polyisoprene (Figure 17) and cis-polybutadiene (Figure 18) model compounds. These figures are similar to the form of Figure 19, which illustrates the change of NR accelerated by CBS. The work of Lautenschlaeger [71] used the same basic approach to study CBS sulfurization of natural rubber, and found results similar to those from the work of Skinner.

Morrison and co-workers used model compounds based on 2-methyl-2-pentene to analyze the behavior of natural rubber accelerator systems during the induction, cure and reversion regimes [4,66-68]. Their first work looked at the sulfurization of 2-methyl-2-pentene with MBTS and MDB [67]. This work concluded that zinc oxide plays a key role in sulfurization and crosslink formation, as in the absence of zinc little sulfurization and almost no crosslinking occurred.

McSweeney and Morrison studied the thermal stability of monosulfidic crosslinks [66] at various temperatures in the presence of different additives. They concluded that the order of stability of monosulfidic crosslinks is:
In another study Morrison [68] analyzed the reactivity of the rubber-bound intermediates under a variety of model vulcanization conditions. Methylene sulfur attachment was found to be more reactive than methyl substitution. Within the methylene substitution structures, B-type structures were found to exhibit greater reactivity than A-type structures. Yet another study analyzed the effect of temperature on the stability of these model compound structures [4]. They also concluded that A-type structures exhibit greater stability than B-type structures.

In these studies Morrison also examined the role of zinc in the vulcanization process. They found that zinc complexes catalyze the formation of crosslink structures from pendant groups, and that zinc complexes also catalyze crosslink reduction [4]. Additionally, Morrison concluded that the reaction of two rubber-bound intermediates results in network formation, as opposed to reaction of 1 rubber molecule with a rubber-bound intermediate [68].
Duchacek also performed kinetic studies to elucidate cure reactions. His study into the effect of temperature on the kinetic constants lead Duchacek to categorize three different kinetic steps; fast crosslinking, slow crosslinking, and degradation [57] as can be seen in Figure 20. He concluded that the slow crosslinking formation was related to the formation of ZnDMDC intermediate. Duchacek also concluded that the fast crosslinking reaction was mainly ionic, while the slow crosslinking and degradation reactions were principally radical in nature.

A kinetic scheme has been proposed by Coran for the vulcanization process [30]:

\[
\begin{align*}
A & \xrightarrow{k_1} B & B & \xrightarrow{k_2} B^* & \xrightarrow{k_3} \alpha V_u \\
A + B^* & \xrightarrow{k_4} \beta B
\end{align*}
\]

Where:
- A = accelerator
- B = intermediate
- B* = active intermediate (sulfurating agent)
- V_u = crosslink
- $\alpha, \beta$ = constants to adjust stoichiometry

In a second paper Coran used this scheme to explain observed relationships between formulation component concentrations and kinetic rate parameters [72]. In the absence of zinc, the induction time was correlated to the sulfur and MBT concentration, while in the
presence of zinc, the induction time was related to the sulfur, MBT and excess Zn (in excess of amount to form MBT). Based on this, Coran also argued for zinc complex formation as the key component for sulfurization; i.e., B is the zinc complex, and the formation of B is the rate limiting step. In a DSC analysis Huson et al. used this kinetic scheme [24], and also argued for the zinc complex as the key component for formation of network structures.

A rigorous kinetic scheme was developed in the work of Chapman to explain the cure behavior of efficient sulfenamide formulations [74]. To aid in kinetic analysis this work used isotopically-labeled accelerators and sulfur. A kinetic scheme involving formation of pendant groups followed by coupling of two pendant groups to form crosslinks and/or cyclic structures was proposed. This model curve-fit to the cure data well, which Chapman concluded validated the fundamental assumptions of the model. This theory agrees with the work of Morrison discussed previously [68], in which he concluded that two pendant groups react to form crosslink or cyclic structures, as opposed to the reaction of one pendant group with a elastomeric repeat unit.
The use of UV analysis has provided another technique for measuring the sulfur chain length in vulcanizates [32]. This work illustrated that UV can be used to quantify the percent of monosulfidic structures in a vulcanizate. Aarts and co-workers analyzed the CBS cure and the CBS/TMTD cure of NR. They found significant levels of monosulfidic structures in efficient (EV) formulations, but only polysulfidic structures in conventional formulations.

Raman spectroscopy has been used by several authors to analyze vulcanizates. Early work in this area was the work of Coleman, Koenig, and Shelton [25,76-78]. This work used Raman to analyze polybutadiene and natural rubber vulcanized with TMTD, TMTD/S, and MBT and derivatives. They concluded that the main products were dialkenyl sulfides, but they also found evidence for di- and polysulfidic structures, as well as for 5 and 6-membered thioalkene and thioalkane cyclic structures:

\[ \text{CH}_2\text{HC} = \text{CH} \text{CH}_2 \]
\[ \text{CH}_2\text{S} \text{CH}_2 \]

They concluded that isomerization does not vary
directly with percent cure, but that the percent of conjugated dienes does. Analysis of these samples via Raman required careful sample preparation, as fluorescence of commercial elastomeric samples is a major problem. More recently, Ellis et al. used FT-Raman to analyze natural rubber [79]. FT-Raman allows analysis of elastomeric samples with no sample preparation, as fluorescence is less of a problem with FT-Raman. This work did not detect any C-S and S-S bands, which is surprising. They did measure conjugated diene structures, and several structures derived from accelerator complexes.

Infrared spectroscopy, despite its potential for analysis of vulcanized elastomers, has not been widely used. The largest application of infrared spectroscopy to elastomers has been for analysis of the chemical microstructure of the uncured elastomers. Devlin and Mengel extended this approach to measure isomerization after cure [7]. Chen and coworkers have used IR to probe the reversion behavior of natural rubber in the presence [80] and absence [81] of carbon black. This papers concluded that the reversion process for a variety of accelerators is related to the formation of trans-methine units:
Trans-methine structure of NR

They further concluded that carbon black increases the reversion resistance of natural rubber by decreasing the rate of formation of the trans-methine groups.

Solid-state C-13 NMR has proven to be a valuable technique for analysis of the sulfurization structure [8,10,31,73,82,83,87,88]. Through the application of line-narrowing techniques and improved instrumental technology, the sensitivity of C-13 solid-state techniques has increased dramatically. Additionally, through the use of 2-D solution techniques, a better understanding of the spectral information can be had [13,73,83].

One of the earliest applications of C-13 NMR to vulcanized elastomers was the work of Werstler [93]. This work involved cleavage of the crosslinks using ortho-dichlorobenzene followed by solution NMR analysis. This approach, while useful, limits the amount of knowledge of network structure that can be obtained.
Solid-state NMR has been used by several groups for analysis of elastomeric systems. The work of Zaper and Koenig involved analysis of natural rubber [82] and polybutadiene [8] vulcanized with TMTD and sulfenamide (CBS,MOR) accelerators. To aid in peak assignment, model compounds based on A-type and B-type structures were used (Figure 16). Zaper and Koenig concluded that sulfurization of NR and CB resulted in cis-trans isomerization and polysulfidic sulfurization of the types A1, B1 and C1 (Figure 16). They saw no evidence for double bond migration or saturation of the double bond, which had been observed for unaccelerated sulfur systems [8,9,13,82]. Additionally, these works did not observe any monosulfidic structures.

Several other authors have studied the sulfurization of natural rubber [83-85]. Gronski and coworkers have studied vulcanization with TMTD and CBS [84,85]. They have found cis-trans isomerization, and evidence for the monosulfidic and polysulfidic sulfurization products of the A,B and C-types shown in Figure 16. This paper also detected several monosulfidic structures, which are listed in Table VII. Additionally, they have derived a relationship between the NMR measurements of percent sulfurization, mechanical measurements and rubber-elastic theory which
allowed calculation of crosslink density of filled materials by correlation of data with similar unfilled materials.

Krejza and Koenig have used solid-state NMR to study vulcanization of cis-polyisoprene with the sulfenamide accelerator TBBS [88] and the sulfenimide accelerator TBSI [94]. Their work did not detect any isomerization, but did detect specific polysulfidic and monosulfidic sulfurization products shown in Figure 16. One of the more interesting conclusions was the role of sulfur in determining the vulcanization products. Analysis of several formulations with similar extents of cure but varying accelerator/sulfur ratios exhibited identical chemical microstructure. The role of sulfur was in the overall extent of sulfurization, while the accelerator concentration determined the efficiency (crosslink/cyclic ratio) of the formulation.

Krejza et. al. also studied thiuram accelerated vulcanization of butyl rubber [87]. They found significant levels of isomerization, and detected only polysulfidic alkenyl products. Interestingly, the types of sulfurization products in this study and the TBBS and TBSI accelerated analysis were very similar; the structures are listed in Figure 16.
Hirst also studied vulcanization of natural rubber [83]. His conclusions as to the sulfurization products were similar, but not identical, to those of Krejsa and Koenig for TBBS and TBSI vulcanization, and are shown in Figure 16. A summary of the types of structures observed in solid-state C-13 NMR studies in tabulated in Table VIII. The general consensus of the NMR studies is that accelerated sulfur vulcanization results in primarily polysulfidic structures with sulfurization allylic (adjacent) to the double bond. Cis–trans isomerization is common, and moderate to small levels of double-bond migration have also been observed.

Layer used the unique approach of recuring vulcanizates to probe the role of sulfur [89] and accelerators [90] in the curing and reversion process. Layer concluded that sulfur determines the overall amount of reaction, but the accelerator determines the length of sulfur chains. This study concluded that the key reaction was the exchange reaction:
This reaction mechanism is similar to the conclusions of Milligan [62], in which low molecular weight sulfides were found to undergo sulfur exchange reactions in the presence of ZnMBT. Blackman and McCall also analyzed the change in network structure of natural rubber vulcanizates during the aging process [91]. They also concluded that the key component in the aging process is residual accelerator, most notably the zinc-accelerator complexes, which agrees with the work of Layer.
B. SULFURLESS SYSTEMS

Sulfurless vulcanization formulations, also referred to as sulfur-free vulcanization, does not contain elemental sulfur. Sulfurless systems usually contain zinc oxide and stearic acid in the formulation, although this is not always the case. The most widely used sulfurless accelerator is tetramethyl thiuram disulfide (TMTD), although other accelerators such as benzothiazylidithiomorpholidine (BTDM):

\[
\text{CH}_3\text{N}\begin{array}{c|c}
|\text{S} \\
\text{CH}_3
\end{array}
\begin{array}{c|c}
|\text{S} \\
\text{CH}_3
\end{array}
\text{N}\text{CH}_3
\]

\[\text{TMTD}\]

\[
\text{CH}_3\text{N}\begin{array}{c|c}
|\text{S} \\
\text{CH}_3
\end{array}
\begin{array}{c|c}
|\text{S} \\
\text{CH}_3
\end{array}
\text{N}\text{CH}_3
\]

\[\text{BTDM}\]

The sulfur for network formation is thus supplied by the accelerator.

The argument for polar and radical mechanisms has continued into the area of sulfurless systems. A summary of conclusions of various groups is shown in Table IX. ESR studies by several groups [15,25,37,95] have indicated that radical reactions are occurring. The work of Coleman et. al. [25] and Duchacek [96-98] have proposed that the initial formation of sulfurizing
species is ionic in nature, while the actual crosslinking species are radical in nature. It is interesting to note that several other works have proposed ionic or radical mechanisms. With the addition of MBT or sulfenamide derivatives of MBT (which serve as prevulcanization inhibitors) [63,99] Duchacek and co-workers proposed a purely polar mechanism. Kruger and McGill [95] proposed pure radical mechanisms, as did Banerjee [37] and Mitra et. al. [100] for TMTD/ZnO systems. Blokh [15] also proposed a radical mechanism based on ESR analysis, but the work of Coleman et. al. [25] illustrated experimental difficulties in the work of Blokh. The conclusion of Bateman et. al. [3] was the reaction of TMTD and ZnO was polar in nature. Banerjee [42] concluded that in the absence of ZnO the reaction was radical, while in the presence of ZnO it was polar in nature.

Duchacek also performed kinetic analysis of sulfur-donor systems [96]. This work concluded similar results to his study on on accelerated sulfur systems discussed in a previous section. It should be noted the fast crosslinking mechanism was not observed until very high concentrations of TMTD, as can be seen in Figure 21 [96]. This work also illustrates another
important conclusion: the nature of the reaction mechanism can vary greatly due to the exact nature of the vulcanization formulation.

The reaction mechanism for a mixed radical and ionic scheme is shown in Figure 22 [25]. This mechanism illustrates both ionic and radical aspects. Furthermore, it would explain the results of several studies reported in the literature. The mechanism in Figure 22 also explains the conclusion of several authors [42,95,100] that a radical mechanism is operative; the thermolysis of XSxX and the sulfurization reactions are radical reactions. The conclusions of Duchacek et al. [63,99] that TMTD reacts via an ionic mechanism in the presence of MBT or sulfenamide derivatives of MBT can be explained by the formation of the complex [63]:

Duchacek believed that this complex vulcanizes via a
polar pathway as opposed to the radical reactions proposed for the dithiocarbamyl complexes.

The network structure of sulfurless systems are similar to those obtained from accelerated sulfur systems discussed in the preceding section. Raman analysis of the sulfurization products [77] detected the presence of dialkenyl sulfides. Additional Raman bands were assigned to polysulfidic and disulfidic structures, rubber bound accelerator intermediates, and various cyclic sulfides including the thioalkane and thioalkene structures illustrated previously. Solid-state C-13 NMR analysis [84,86] measured a mix of mono-, di- and polysulfidic structures for both crosslink structures and rubber-bound accelerator intermediates. Additionally, the work of Smith et.al. [86] detected saturated sulfurized structures, vicinal (side-by-side sulfurization) structures, and significant levels of cis-trans isomerization. It should be noted that the measurement of significant amounts of rubber-bound intermediates is common for polybutadiene, but not for natural rubber [3]. This explains why the work of Gronski et. al. [84] did not detect significant levels of rubber-bound intermediate, as their work was with sulfur-donor vulcanization of natural rubber.
Another approach for sulfur-donor vulcanization was the use of model compounds. This study by Gregg and Lattimer [92] used the cyclic tetramer cyclohexadeca-1,5,9,13-tetraene (CHT) to model cis-polybutadiene:

![Cyclohexadeca-1,5,9,13-tetraene (CHT)](image)

Their work reached several interesting conclusions on both sulfurization of elastomers and the model compound approach. This work suggested that for butadiene models a minimum of 3 allylic double bonds is required to accurately model the reactivity of polybutadiene. This would question the results of the work of Wolfe et. al. [11,12], which used cyclohexene (single olefinic unit). The work of Gregg and Lattimer agrees well with the results of Smith as to possible network structures. Gregg et. al. measured cis-trans isomerization near the site of sulfurization, mono- and disulfidic crosslinks, vicinal crosslinking, and a
variety of rubber-bound intermediates, which can be seen in Figure 23 [92].

Another technique for sulfurless vulcanization analysis has been the use of DSC coupled with chemical probe/equilibrium swelling analysis [95,101]. The results of this work indicated that zinc oxide dramatically increases the efficiency of vulcanization, but is not required for sulfurization [95]. Additionally, the authors postulate that the accelerator derivative responsible for network shortening reactions is not ZnDMDC, but instead is tetramethyl thiuram monosulfide (TMTM) [101]. This does not agree completely with the work of Frenkel [102], who measured the formation of nickel stearate-TMTD complexes. This work would suggest that ZnDMDC-stearate complexes will form; these complexes as mentioned previously are believed by many to be the actual network maturation agent.
C. BINARY SYSTEMS

Binary accelerator systems is an aspect of vulcanization that has been generating increasing interest in recent years. Due to the increased complexity of these systems, only recently have papers begun to fully probe the intricacies of binary systems.

A binary accelerator system refers to the use of two (or more) accelerators in a given formulation. Some of the more widely used accelerators for binary systems are shown in Table X [103]. The motivation for this can be seen in Figures 24-26 [104]. In these figures the benefits of binary systems can be seen in butyl, EPDM, and NR rubber formulations. The synergistic behavior of these systems has been studied by several authors [103-109].

Technically, the use of binary accelerators is quite old. Many amines such as diphenylguanidine (DPG) are used in combination with other accelerators such as MBT or sulfenamides to activate the vulcanization reaction. However, present-day binary accelerators systems usually consist of benzothiazole and thiocarbamate derivatives. Additionally, MBT and
sulfenamides are often added to thiuram systems to increase the scorch delay of these systems [110,111]. This was discussed in the previous section dealing with the accelerator behavior during the scorch delay period.

There have been several methods of analyzing the vulcanization behavior of binary accelerators. It is believed [103-109] that the improved properties of binary systems derives from the formation of combination accelerator complexes. One method of analysis of these complexes is to measure mechanical or physical properties as a function of accelerator ratio [104,109] and correlate the optimum property ratio with the complex formation. This approach, which is used by Layer, suggests the formation of specific complexes. An example of this is the formation of the complex between OBTS and OTOS, Layer suggests that the actual vulcanizing complex for the OBTS/OTOS system is the complex [104]:

![Chemical structure diagram]
Another method of analyzing binary systems has been extraction of the extra-network material followed by HPLC analysis of the extract. This approach has been followed by Basu and co-workers [103,105-107]. Their conclusions are similar to those in Layer's work; they detected several products resulting from the cross reaction of the binary accelerators.
IV. SUMMARY

This work has summarized the present understanding of the fundamental science and chemistry of rubber vulcanization. The future of this area holds much potential. Recent studies have begun to fully elucidate the accelerator and accelerator complex chemistry, and definitively answer questions that have been open for debate for many years. Additionally, the understanding of the network structure is rapidly progressing through advances in analytical techniques. The largest area of future research will be the use of multiple experimental techniques to fully elucidate and understand the relationship between accelerator chemistry and specific network structures formation. With this knowledge, it will then be possible to molecularly engineer vulcanizates with specific properties.
V. REFERENCES


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63. V. Duchacek, J. Appl. Poly. Sci., 16, 3245 (1972)


83. R.C. Hirst, Rubber Division Meeting, Detroit, MI, Oct. 1991, Paper No. 69


90. R. Layer, Rubber Chem. Technol., 65, Accepted (1992)


96. V. Duchacek, Rubber Chem. Technol., 48, 945 (1975)


111. C.K. Das, W. Millns, Rubber India, 30, 13 (1978)
\begin{table}
\centering
\caption{SEVERAL COMMON ACCELERATORS USED IN SULFUR VULCANIZATION [6]}
\begin{tabular}{lll}
\hline
\textbf{Compound} & \textbf{Abbreviation} & \textbf{Structure} \\
\hline
Benzothiazoles & & \\
2-mercaptobenzothiazole & MBT & \\
2,2'-dithiobisbenzothiazole & MBTS & \\
\hline
Benzothiazolesulfenamides & & \\
\textit{N}-cyclohexylbenzothiazole-2-sulfenamide & CBS & \\
\textit{N}-t-butylbenzothiazole-2-sulfenamide & TBBS & \\
2-morpholinothiobenzothiazole & MBS & \\
\textit{N}-dicyclopentylbenzothiazole-2-sulfenamide & DCBS & \\
\hline
Dithiocarbamates & & \\
tetramethylthiuram monosulfide & TMTM & \\
tetramethylthiuram disulfide & TMTD & \\
\hline
zinc diethyldithiocarbamate & ZDEC & \\
\hline
Amines & & \\
diphenylguanidine & DPG & \\
di-o-tolylguanidine & DOTG & \\
\hline
\end{tabular}
\end{table}
### TABLE II

<table>
<thead>
<tr>
<th>Property</th>
<th>Change with increase in degree of crosslinking</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Properties dependent only on degree of crosslinking</strong></td>
<td></td>
</tr>
<tr>
<td>stiffness (modulus)</td>
<td>increase</td>
</tr>
<tr>
<td>hardness</td>
<td>increase</td>
</tr>
<tr>
<td><strong>Properties partly dependent on degree of crosslinking</strong></td>
<td></td>
</tr>
<tr>
<td>breaking elongation</td>
<td>decrease</td>
</tr>
<tr>
<td>resilience</td>
<td>increase</td>
</tr>
<tr>
<td>heat build-up</td>
<td>decrease</td>
</tr>
<tr>
<td>solvent swelling</td>
<td>decrease</td>
</tr>
<tr>
<td>creep, stress relaxation</td>
<td>decrease</td>
</tr>
<tr>
<td>set</td>
<td>decrease</td>
</tr>
<tr>
<td>abrasion resistance</td>
<td>increase</td>
</tr>
<tr>
<td>fatigue cracking</td>
<td>increase</td>
</tr>
<tr>
<td>low-temperature crystallization</td>
<td>decrease in rate</td>
</tr>
<tr>
<td>tensile strength, tear strength</td>
<td>increase, then decrease</td>
</tr>
</tbody>
</table>

Taken from Reference 4.
### TABLE III

**Influence of Di- and Polysulfide Crosslinks on Properties**

<table>
<thead>
<tr>
<th>Property</th>
<th>Change with increase in proportion of di- and polysulfides</th>
</tr>
</thead>
<tbody>
<tr>
<td>creep, stress relaxation</td>
<td>increase</td>
</tr>
<tr>
<td>set</td>
<td>increase</td>
</tr>
<tr>
<td>incremental swelling</td>
<td>increase</td>
</tr>
<tr>
<td>tensile strength, tear strength</td>
<td>increase</td>
</tr>
<tr>
<td>resilience</td>
<td>increase</td>
</tr>
<tr>
<td>fatigue failure</td>
<td>decrease</td>
</tr>
<tr>
<td>heat resistance</td>
<td>decrease</td>
</tr>
<tr>
<td>thermal aging resistance</td>
<td>decrease</td>
</tr>
</tbody>
</table>

Taken from Reference 4.
### TABLE IV

<table>
<thead>
<tr>
<th>Property</th>
<th>Change with increase in degree of modification</th>
<th>Olefinic*</th>
<th>Cyclic sulfide</th>
<th>Pendent group</th>
</tr>
</thead>
<tbody>
<tr>
<td>resilience</td>
<td>decrease</td>
<td>decrease</td>
<td>little effect?</td>
<td></td>
</tr>
<tr>
<td>strength&lt;sup&gt;a&lt;/sup&gt;</td>
<td>decrease</td>
<td>decrease</td>
<td>little effect?</td>
<td></td>
</tr>
<tr>
<td>fatigue failure</td>
<td>decrease</td>
<td>decrease</td>
<td>little effect?</td>
<td></td>
</tr>
<tr>
<td>swelling in hydrocarbon oils</td>
<td>decrease?</td>
<td>decrease</td>
<td>decrease?</td>
<td></td>
</tr>
<tr>
<td>oxidative aging resistance</td>
<td>decrease</td>
<td>decrease</td>
<td>decrease?</td>
<td></td>
</tr>
<tr>
<td>low-temperature crystallization</td>
<td>rate decrease</td>
<td>rate decrease</td>
<td>little effect</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>Includes conjugated diene and triene groups and cis, trans-isomerized units.

<sup>b</sup>Especially high-temperature strength.

Taken from Reference 4.
### TABLE V

**RADICAL/POLAR CONCLUSIONS OF SEVERAL AUTHORS VIA USE OF RADICAL SCAVENGERS**

<table>
<thead>
<tr>
<th>Author</th>
<th>System</th>
<th>Conclusion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Thiuram Disulfide/S</td>
<td>Predominantly Polar</td>
</tr>
<tr>
<td></td>
<td>Dithiocarbamate/S</td>
<td>Predominantly Polar</td>
</tr>
<tr>
<td></td>
<td>Thiazole Disulfide/S</td>
<td>Mixed polar/radical</td>
</tr>
<tr>
<td></td>
<td>Sulfenamide/S</td>
<td>Mixed polar/radical</td>
</tr>
<tr>
<td>Duchacek [33,35]</td>
<td>TMTD/S</td>
<td>Polar initiation Radical crosslinking</td>
</tr>
<tr>
<td>Morita, Young [34]</td>
<td>Sulfenamide/ Sulfur/ZnO/ Stearic Acid</td>
<td>Mixed polar/radical</td>
</tr>
<tr>
<td>Mechanism</td>
<td>System</td>
<td></td>
</tr>
<tr>
<td>---------------------</td>
<td>-------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>Radical:</td>
<td>NR/TMTD [42]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>NR/TMTD/S [42]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>NR/CBS/S [49]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SBR/MBT/S [45]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>NR/MBT/S [46]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>NR/MBT/S in presence of carbon black [43]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>NR/MDB/S/TMTD [39]</td>
<td></td>
</tr>
<tr>
<td>Mixed Radical /Polar:</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NR/CBS/S/ZnO/Stearic Acid [49]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SBR/DPG/S/ZnO/Stearic Acid [47]</td>
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</tr>
<tr>
<td></td>
<td>NR/MBT/TMTD/S [41]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SBR/CBS/S [44]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SBR/CBS/S/ZnO/Stearic Acid [44]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>NR/MBT/DPG/S [40]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>NR/DPG/S/ZnO/Stearic Acid [48]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>NR/MDB/S/TMTD/ZnO/Stearic Acid [39]</td>
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</tr>
<tr>
<td>Polar:</td>
<td>NR/TMTD/S/ZnO/Stearic Acid [42]</td>
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</tr>
<tr>
<td></td>
<td>NR/MBT/TMTD/S/ZnO/Stearic Acid [41]</td>
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</tr>
<tr>
<td></td>
<td>NR/MBT/DPG/S/ZnO/Stearic Acid [40]</td>
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<td></td>
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<td>SBR/DPG/S [47]</td>
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<td></td>
<td>NR/MBT/S/ZnO/Stearic Acid [46]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>NR/MBT/S/ZnO/Stearic Acid in the presence of carbon black [43]</td>
<td></td>
</tr>
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<td></td>
<td>SBR/MBT/S/ZnO/Stearic Acid [45]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>NR/TMTD/ZnO [42]</td>
<td></td>
</tr>
<tr>
<td>Structure</td>
<td>Accelerator</td>
<td></td>
</tr>
<tr>
<td>-----------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>B2SB2</td>
<td>CBS</td>
<td></td>
</tr>
<tr>
<td>B2SC1</td>
<td>CBS, TMTD</td>
<td></td>
</tr>
<tr>
<td>B1SA1</td>
<td>CBS, TMTD</td>
<td></td>
</tr>
<tr>
<td>B1SC1</td>
<td>TMTD</td>
<td></td>
</tr>
<tr>
<td>A1SA1</td>
<td>CBS</td>
<td></td>
</tr>
<tr>
<td>A1SC1</td>
<td>CBS, TMTD</td>
<td></td>
</tr>
</tbody>
</table>
TABLE VIII

SUMMARY OF NETWORK STRUCTURES FROM ACCELERATED SULFUR VULCANIZATION OF NATURAL RUBBER AND CIS-POLYISOPRENE MEASURING USING C-13 NMR

<table>
<thead>
<tr>
<th>Structure</th>
<th>Reference No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1Sx-</td>
<td>82, 84, 85, 87, 88, 94</td>
</tr>
<tr>
<td>A2Sx-</td>
<td>84, 85, 94</td>
</tr>
<tr>
<td>B1Sx-</td>
<td>82, 84, 85, 87, 88, 94</td>
</tr>
<tr>
<td>B2Sx-</td>
<td>84, 85</td>
</tr>
<tr>
<td>ClSx-</td>
<td>82, 84, 85, 88, 94</td>
</tr>
<tr>
<td>Cis/trans isomerization</td>
<td>82, 84, 85, 87</td>
</tr>
</tbody>
</table>
TABLE IX

MECHANISTIC CONCLUSIONS OF SEVERAL AUTHORS FOR SULFUR-DONOR VULCANIZATION

<table>
<thead>
<tr>
<th>Author</th>
<th>System</th>
<th>Conclusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Duchacek, Bhattacharyya,</td>
<td>TMTD/ZnO/ Sulfenamides</td>
<td>Ionic</td>
</tr>
<tr>
<td>and Kuta [99]</td>
<td>TMTD</td>
<td>Ionic initiation, Radical crosslinking</td>
</tr>
<tr>
<td>Duchacek [63]</td>
<td>TMTD/ZnO/ Thiourea</td>
<td>Ionic initiation, Radical crosslinking</td>
</tr>
<tr>
<td>Duchacek [97,98]</td>
<td>TMTD/ZnO</td>
<td>Inconclusive</td>
</tr>
<tr>
<td>Shelton, McDonel [14]</td>
<td>TMTD/ZnO</td>
<td>Radical</td>
</tr>
<tr>
<td>Blokh [15]</td>
<td>TMTD/ZnO</td>
<td>Radical</td>
</tr>
<tr>
<td>Kruger, McGill [95]</td>
<td>TMTD/ZnO</td>
<td>Radical crosslinking</td>
</tr>
<tr>
<td>Banerjee [37]</td>
<td>TMTD/ZnO/ Various amines</td>
<td>Radical crosslinking</td>
</tr>
<tr>
<td>Mitra, Das, Mills [100]</td>
<td>TMTD/ZnO</td>
<td>Radical</td>
</tr>
<tr>
<td>Chemical name</td>
<td>Abbreviation</td>
<td>Structure</td>
</tr>
<tr>
<td>-------------------------------------</td>
<td>--------------</td>
<td>------------------------------------------------</td>
</tr>
<tr>
<td>1. Cyclohexyldibutylamine</td>
<td>CDBA</td>
<td>![Structure Image]</td>
</tr>
<tr>
<td>2. Cyclohexylthiobenzothiazole</td>
<td>CDB</td>
<td>![Structure Image]</td>
</tr>
<tr>
<td>3. Cyclohexyldibenzopyrrole</td>
<td>CDBP</td>
<td>![Structure Image]</td>
</tr>
<tr>
<td>4. Cyclohexyldiethylamine</td>
<td>CDEA</td>
<td>![Structure Image]</td>
</tr>
<tr>
<td>5. Cyclohexyldiisopropylamine</td>
<td>CDIPA</td>
<td>![Structure Image]</td>
</tr>
<tr>
<td>6. Cyclohexylthiophenylamine</td>
<td>CDPA</td>
<td>![Structure Image]</td>
</tr>
<tr>
<td>7. Cyclohexylthiomorpholine</td>
<td>CM</td>
<td>![Structure Image]</td>
</tr>
<tr>
<td>8. Cyclohexylthiopiperidine</td>
<td>CP</td>
<td>![Structure Image]</td>
</tr>
<tr>
<td>9. Cyclohexylthiopyrroldine</td>
<td>CP</td>
<td>![Structure Image]</td>
</tr>
<tr>
<td>10. N-cyclopentamethylene-2-benzothiazole sulphenamide</td>
<td>CPBS</td>
<td>![Structure Image]</td>
</tr>
</tbody>
</table>
### TABLE X (continued)

<table>
<thead>
<tr>
<th>Chemical name</th>
<th>Abbreviation</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>11. Bis(Cyclopentamethylene) thiuram disulfide (^5)</td>
<td>CPTD</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>12. N-Cyclopentamethylene thiocarbamyl-2-benzo-thiazyl disulfide</td>
<td>CTBD</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>13. N-Cyclopentamethylene-thiocarbamyl-(N)-Cyclopentamethylene sulfinamide (^a)</td>
<td>CTCS</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>14. N-Cyclohexylthiophthalimide</td>
<td>CTP</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>15. Dibenzopyrrole</td>
<td>DBP</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>16. Dicyclohexylthio-piperazine</td>
<td>DCDP</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>17. Di-(\beta)-naphyl-(\alpha)-phenylene-diamino</td>
<td>DNPD</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>18. 2-Mercaptobenzothiazole</td>
<td>MBT</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>19. Dibenzothiazyl disulfide</td>
<td>MBTS</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>20. 4-Morpholinyl-2-benzothiazole disulfide (^1,2)</td>
<td>MDB</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>21. N-Oxyl-thylene-2-benzothiazole sulfinamide</td>
<td>ODTS</td>
<td><img src="image" alt="Structure" /></td>
</tr>
</tbody>
</table>
TABLE X (continued)

<table>
<thead>
<tr>
<th>Chemical name</th>
<th>Abbreviation</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>22. N-Oxydiethylene-thiocarbamyl-2-benzothiazyl disulfide</td>
<td>OTBD</td>
<td><img src="image1" alt="Structure" /></td>
</tr>
<tr>
<td>23. N-Oxydiethylene-thiocarbamyl cyclohexyl disulfide</td>
<td>OTCD</td>
<td><img src="image2" alt="Structure" /></td>
</tr>
<tr>
<td>24. Bis(oxydiethylene) thiuram disulfide</td>
<td>OTD</td>
<td><img src="image3" alt="Structure" /></td>
</tr>
<tr>
<td>25. N-Oxydiethylene-thiocarbamyl-N-oxydiethylene sulfenamide</td>
<td>OTOS</td>
<td><img src="image4" alt="Structure" /></td>
</tr>
<tr>
<td>26. N-phenyl-N'-isopropyl-(p)-phenylenediamine</td>
<td>PIPPD</td>
<td><img src="image5" alt="Structure" /></td>
</tr>
</tbody>
</table>
Effects of crosslink density on the NR vulcanizates of CV, and EV systems with DPG as accelerator (●, CV; ○, EV).

Figure 1: Relationship between crosslink density and tensile strength for DPG-NR vulcanizate in conventional and efficient systems [5].
Figure 2: Cure rheograph illustrating the three main periods of vulcanization: scorch delay (I), cure (II), and reversion (III) [6].
Figure 3: Generalized mechanism of vulcanization [4].
Figure 4: Proposed radical mechanism for unaccented sulfur vulcanization [3].
Figure 5: Proposed radical mechanism for isomerization and double bond migration in pure sulfur vulcanization [3].
Figure 6: Proposed polar mechanism for unaccelerated sulfur vulcanization [3].
INITIATION: Polysulfide P $\rightarrow$ TSz+ + TSy-

PROPAGATION: TSz+ + RH $\rightarrow$ TSzRH+

$H^-_{\text{transfer}}$ $\rightarrow$ TSzR + RH$_2$+ $\rightarrow$ TSzRH$_2$ + R+

RH$_2$+ $\rightarrow$ S$_8$ $\rightarrow$ RH$_2$S + TSz+

R+ $\rightarrow$ RSz+

TERMINATION: RH$_2$+ + TSz+ $\rightarrow$ Nonchain carriers

Figure 7: Generalized version of polar mechanism for pure sulfur vulcanization allowing for either proton or hydride transfer [3].
Figure 8: Mechanism of cyclic formation for polar mechanism of unaccelerated sulfur vulcanization [3].
Figure 9: Model compounds used for analysis of unaccelerated sulfur vulcanization [3,11].
Figure 10: Sulfurization structures found in model compound unaccelerated sulfur vulcanization [3,11].
Figure 11: Network structures found in unaccelerated sulfur NR and BR vulcanizates [8-10,13].
Figure 12: Fate of curatives during MBT-accelerated sulfur cure of NR [27].
Figure 13: Fate of accelerator system during cure of efficient sulfinimide system [29].
Figure 14: Differences in reactivity of various elastomers to radical oxidation. initiated by MBT radical [50].
Figure 15: Rheograph illustrating formation of vulcanization inhibitors in situ [64].
Figure 16: Sulfurization network structures predicted from model compound work [70,71].
Figure 17: Sulfides found in 2-methyl-2-pentene sulfurization as a function of cure time [70].
Figure 18: Sulfides found in cis-hex-3-ene sulfurization as a function of cure time [70].
Figure 19: Sulfurization in CBS accelerated vulcanization of NR as function of cure time [70].
EQUATION USED FOR KINETIC ANALYSIS:

\[ E = X(1 - e^{-kt}) + Y(1 - e^{-kt}) + Z(1 - e^{-kt}) \]

Figure 20: Kinetic analysis of vulcanization of cis-polybutadiene exhibiting slow and fast crosslinking, and degradation [57]. Formulation: IR 100 phr, ZnO 5 phr, TMTD 50 phr.
Figure 21: Change in ODR cure traces with TMTD concentration [96]. Base formulation: Pale crepe 100 phr, ZnO 5 phr, TMTD variable.
Figure 22: Proposed radical/polar mechanism for sulfur-donor vulcanization [25].
Figure 23: Crosslink and cyclic structures found in sulfur-donor-CB model compound vulcanization [92].
Figure 24: Effect of ratio of OBTS/OTOS ratio on 300% modulus of butyl rubber [104].
Figure 25: Effect of ratio of OBTS/OTOS ratio on 300% modulus of EPDM rubber [104].
Figure 26: Effect of ratio of OBTS/OTOS ratio on 300% modulus of natural rubber [104].
CHAPTER II

SOLID-STATE C-13 NMR STUDIES OF TERT-BUTYL BENZOTHIAZOLE SULFENAMIDE (TBBS) ACCELERATED SULFUR VULCANIZATION OF CIS-POLYISOPRENE
I. INTRODUCTION

Synthetic cis-polyisoprene is a high volume elastomer with many applications ranging from tires to automotive hoses and gaskets [1-3]. The wide applicability of this material has provided the impetus for the significant volume of analysis aimed at elucidating the physical and chemical properties of this elastomer vulcanized in a wide variety of curing systems. This research has lead to extensive work in attempting to understand the chemistry of vulcanization [1,2,4-18]. There is a strong desire to understand the vulcanization chemistry and resulting structures, and to relate this knowledge to end-use properties [2,19,20]. Work in this area has included relating physical properties such as tensile strength, tear strength, thermal stability, etc., to the chemical microstructure of the vulcanizate. One major drawback of this approach has been the limited ability to directly measure the changes in the chemical microstructure. Due to limits of sensitivity and problems with sampling techniques which derive from the insolubility of cured elastomers, analytical techniques until recently have not achieved wide success in analyzing vulcanizate microstructure [21-43].
Much of the early work in analyzing rubber vulcanization utilized indirect methods including equilibrium swelling measurements, chemical probe work, stress-strain measurements, model compound work, and analysis of residual curing agents [2,4-18,44-51]. The disadvantage of these approaches is that they do not directly measure the number and type of crosslinks and suffer from problems with extrapolation to actual elastomers.

Spectroscopic techniques have been applied to this problem recently with much greater success [26-43]. With the advent of Fourier-Transform NMR and improvements in instrument technology, the study of insoluble materials has become a much easier proposition. Carbon-13 NMR is potentially useful for analysis of insoluble polymers through the ability to discriminate between uncured and cured resonances. What was needed to apply FT NMR to elastomers was the development of solid-state line narrowing techniques and improved sensitivity. The line narrowing has been achieved through several methods, including magic angle sample spinning and gated high power decoupling. Magic angle sample spinning removes chemical shift anisotropy, while gated high power decoupling removes dipolar broadening effects. Improved sensitivity has
been achieved through signal averaging and the development of high field magnets. The signal intensity is proportional to the 1.75 power of the magnetic field; thus, increasing the field dramatically increases the sensitivity.

Specifically, the purpose of this study was to analyze the chemical microstructure of vulcanized cis-polyisoprene as a function of extent of cure and accelerator/sulfur ratio. To perform this study, a conventional, semi-efficient and efficient vulcanization system was analyzed by C-13 solid-state NMR. The formulations, shown in Table I, differed only in the accelerator/sulfur ratio. The accelerator used was tert-butyl benzothiazole sulfenamide, which is manufactured by Monsanto Corp. and is known under the trade name Santocure NS. All three systems were formulated such that the ultimate extent of cure in each system was identical. Additionally, the time at which sulfurization started and the time at which the system reached full cure was identical, though the rate at which sulfurization occurred varied between the three formulations.
II. EXPERIMENTAL

All samples for this study were supplied by the Rubber Chemicals Division of Monsanto Corporation. A Monsanto rheometer was modified so as to include several small disks on the outer edge of the rheometer mold. These disks were of the proper diameter to be used in a 7 mm zirconia rotor for analysis for solid-state NMR. This mold ensured that the exact extent of cure for the samples would be known, as the extent of cure was measured simultaneously with sample preparation.

Samples were cured for times ranging from 30 minutes to 300 minutes for the conventional system (Formulation 2B) and from 42 minutes to 105 minutes for the semi-efficient and efficient systems (Formulations 3B and 4B). The rheometer traces for each formulation are shown in Figure 1. The conventional system was analyzed for a greater number of cure times to determine the sulfurization products for this system. These results were then used to analyze the spectra from the semi-efficient and efficient vulcanization systems. Samples were cured at 140°C.
All NMR measurements were performed on a Bruker MSL 300 at a carbon frequency of 75.47 MHz. Measurements were performed at room temperature on a CP/MAS probe using magic angle sample spinning and gated high power decoupling. One sample of the conventional formulation was also analyzed at 180 °C. Quantitative measurements were performed using 8000 scans and a recycle delay of 6 seconds, while for non-quantitative measurements a recycle delay of 2 seconds was used and 30000 transients were collected. The data was transferred from the MSL 300 to a Microvax II using Ethernet, where the data was analyzed using in-house software developed in FORTRAN 77.

Quantitative measurements in C-13 NMR require that the recycle delay be longer than 5 times the longest T1 spin-lattice relaxation time. T1 values were measured for the cis-polyisoprene and trans-polyisoprene carbons and are shown in Table II. As can be seen from Table II, the recycle delay of 6 seconds is longer than 5 times the longest T1 value of the cis carbons, and results in less than 1 percent loss of signal for two of the trans carbons. These values agree well with literature values [52]. The assumption was made that the vinyl carbons would show similar T1 relaxation behavior to the cis and trans carbons.
Three samples of the conventional formulation were extracted using a 2:1 mixture of p-dioxane and acetonitrile. All other samples were not extracted.

Equilibrium swelling measurements were performed using n-decane as a solvent. Samples were swollen for 1 day, and the measurements repeated over several days. The polymer-solvent interaction parameter is 0.43, and the molecular weight of the uncured rubber is 219,000. The Moore-Watson calibration curve for chain entanglements was used.
III. RESULTS

The C-13 NMR spectra of all three formulations are shown in Figure 2. These spectra look very similar, but when the small resonances are examined differences can be detected.

The trans isomer, shown in Figure 3, was measured by following the peaks at 40 and 16 ppm, and was found to remain constant for all three formulations at all cure times. Several resonances appeared in the cured material which were absent in the uncured material. A new sulfurization resonance appeared at 51 ppm at short cure times in all three systems. A new resonance at 38 ppm varied in concert with the peak at 51 ppm, but was of lower intensity as is shown in Figure 4. Both these resonances weakened and disappeared at longer cure times, and new resonances appeared at 45, 58, 64, 17, 14 and 12 ppm. These peaks are shown in Figures 5 and 6. The resonances at 51 and 45 ppm were both split into doublets. The resonance at 64 ppm was a weak resonance which was detectable in the conventional system, barely discernible in the SEV system, and could not be detected in the EV system. The dominant sulfurization resonances at long cure times were the peaks at 58 and 45 ppm. The intensities of the new
resonances were strongest in the conventional system and weakest in the EV system. No reaction of the vinyl units occurred, nor was there any evidence of saturation, double bond migration, or chain scission. The measured amount of benzothiazole groups increased more slowly than the amount of benzothiazole groups added to the system. The peak due to benzothiazole groups at 152 ppm was found to disappear upon extraction of the samples.
IV. DISCUSSION

A. CONVENTIONAL SYSTEM

At low cure times the only new resonance observed was the doublet at 51 ppm shown in work [37-39], it was possible to assign this peak to the polysulfidic structure A1c shown in Figure 3. The assignment of this peak aided in the assignment of the resonance at 45 ppm shown in Figure 5. This peak, which does not appear until longer cure times, is the monosulfidic version of A1c. This results agrees with past work [37]. The behavior of these peaks with cure is shown in Figures 6 and 7. Figure 6 illustrates that the amount of polysulfidic A1c increases rapidly at short cure times, reaches a maximum at 38-40 minutes, and then decreases more slowly, ultimately disappearing by 70 minutes cure. Correspondingly, the resonance at 45 ppm in Figure 7 increases rapidly initially, and then more slowly up to 300 minutes cure time. Initially, polysulfidic A1c forms and then reduces to monosulfidic A1c, while at longer cure times monosulfidic A1c is formed directly.
The appearance of the new resonances at 64 and 58 ppm shown in Figure 5 coincides with the appearance of the new resonances at 17, 14 and 12 ppm shown in Figure 8. The changes of the sulfurization resonances at 58 ppm and 64 ppm with cure time are shown in Figure 7. The appearance of the three new resonances upfield at 17, 14 and 12 ppm suggests that the sulfurization products are producing a gamma shift in the methyl carbons. The C1 carbon would produce gamma shifts in this region; based on this result and chemical shift calculations shown in Table III we can assign the peak at 58 ppm to a polysulfidic B1c, and the resonance at 64 ppm to polysulfidic B1t. The change of the carbon at 14 ppm is plotted against the change in the alpha carbon at 64 ppm in Figure 9. The linear correlation confirms the assignment of this peak to the gamma shift of the methyl carbon (trans) with formation of B1t. The peaks at 17 and 12 therefore must arise from B1c; this is confirmed by Figure 10 which shows a fairly linear correlation between the peaks at 17 and 12 ppm versus the peak at 58 ppm. The magnitude of this gamma shift and the appearance of two distinct resonances suggest that the methyl carbon "sees" two distinct conformational isomers. A similar splitting was seen for the alpha carbons at 51 and 45 ppm, although of a much smaller nature (0.5 ppm). Thus, the analysis of
the splittings became an important part of this work.

The source of the splittings of the alpha and gamma carbons was analyzed by model compound studies and variable temperature work. The most likely cause of such resonance splittings is distinguishable conformations; that is, sufficiently slow rotation between conformations such that they can be distinguished by NMR. The spectrum of the 180 minute cure sample was collected at 80 °C. No collapse of these peaks into a singlet occurred, which suggested a very high energy barrier of rotation. Analysis of solution work for model compounds for this structure (AlSxAl, [39], Figure 11) indicates that for x equal to 2, a doublet was observed as can be seen in Table IV, but for x equal to 1 or 3 only a singlet is observed. This splitting is due to rotational and distance effects. If the crosslink is monosulfidic, then the isoprene rotation cannot occur due to the limited distance between chains. For trisulfidic chains or greater, the interchain distance is too great for the differences in shielding to split the NMR resonance. For a disulfidic crosslink both conformers exist, but the interchain distance is small enough that the chemical shifts of the alpha carbons are distinguishable. It was also interesting to note for
the disulfidic pendant group only a singlet was observed. For a pendant group there is less hindrance to rotation; therefore the conformers are not distinguishable by NMR.

The new resonance at 38 ppm has been assigned to the carbon adjacent to the sulfurized carbon of A1c. What is unusual about this carbon is that the behavior of this carbon follows the behavior of the resonance at 51 ppm, but the intensity is significantly lower. This suggests a splitting of the beta carbon into two resonances as was observed for other carbons.

The appearance of a doublet at 51 ppm for polysulfidic A1c leads to the conclusion that the initial sulfurization is at least partially disulfidic for this resonance. The splitting of the peak at 45 ppm, while not predicted by the model compound work, suggests that when the polysulfidic structure reduces to a monosulfidic structure that the mechanism of reduction does not allow rotation of the conformers to a single low energy structure. Model compound work did not show a doublet since it was highly unlikely to enter the high energy conformation. For elastomers, the situation is complicated by the influence of the attached isoprene units.
It should be noted that these assignments disagree with a recent C-13 NMR study [40]. In this study the splittings at 51 and 45 ppm are assigned as unique resonances for different sulfidic structures. If the peaks at 51 and 45 ppm are taken as two distinct overlapped resonances, it would be highly unusual for the signal intensity to vary in such a coherent fashion if the structures are unrelated as suggested. The general change in intensity of the bands at 51 and also at 38 ppm agrees well with our studies.

The band at 64 ppm is also assigned differently in the work of Gronski et. al. [40]. Peaks further downfield than 60 ppm were assigned to oxidation products. If this is the case, then carbonyl bands should also be in evidence. In these samples no evidence was seen for carbonyl structures.

Figure 12 shows the change in the amount of trans and vinyl carbons with cure. The percentages of trans and vinyl were followed using previously assigned peaks [28] at 40 and 16 ppm for trans and 148, 112, 48 and 18 ppm for vinyl. The measured values agree with literature values [31] for the amount of trans and vinyl in unreacted Natsyn 2200, which is 1.4% trans and 0.5% vinyl. Solution work also confirmed the literature and solid-state values. Thus, cis-trans
isomerization does not occur in any of the formulations. Much of the work in the past has indicated that substantial amounts of isomerization occur during vulcanization [2,36-43,53]. The lack of cis-trans isomerization suggest that vulcanization does not proceed through the formation of a stable radical or ionic species.

Also of interest was the ability to measure the amount of accelerator present. The benzothiazole groups were measured through the peak at 152 ppm, which arises from a carbon in the aromatic ring. Figure 12 illustrates the change in the amount of benzothiazole groups present as a function of cure time. The amount of benzothiazole groups in the formulation is 0.27%, which agrees well with our findings. Extraction of three samples (42, 48, and 70 minutes) followed by subsequent NMR analysis illustrated that the benzothiazole resonance disappears upon extraction as is shown in Figure 13. Thus, most of the benzothiazole groups are in some form of activated accelerator.

It is also interesting to note the behavior of the sulfurization products A1c mono and polysulfidic. At low cure times the only sulfurized structure is polysulfidic A1c; thus, all crosslinks are of the type A1c-Sx-A1c. At long cure times the only monosulfidic
structure is Alc, indicating that all monosulfidic crosslinks are of the form Alc-S-Alc. This is consistent with the previous discussion that the reduction of rank proceeds through a concerted mechanism; if a stable intermediate were involved, then there should be rearrangement to form a variety of monosulfidic crosslink structures. Initially, the monosulfidic crosslinks are formed by reduction of polysulfidic crosslinks; at longer cure times monosulfidic sulfurization products form directly.
B. SEMI-EFFICIENT SYSTEM

This system shows nearly identical behavior as observed in the conventional system. At short cure times the dominant sulfurization product is polysulfidic Alc, while at longer cure times the products are polysulfidic Blc and B1t, and monosulfidic Alc. The overall ratios of the three products is very similar, with Alc and Blc being the dominant structures. Cis-trans isomerization is not observed, nor is reaction of the vinyl structure as shown in Figure 14.
C. EFFICIENT SYSTEM

For this system we see similar behavior as observed in both the conventional and semi-efficient systems, with polysulfidic A1c forming at low cure times, and polysulfidic B1c and B1t and monosulfidic A1c at long cure times. Cis-trans isomerization is not observed, nor is any reaction of the vinyl structure, as can be seen from Figure 14.
D. MECHANISTIC COMMENTS

All three accelerator/sulfur ratios were found to produce a similar chemical microstructure, which is unexpected. Figure 14 begins to produce some insight into this phenomena. In this figure we see that the amount of benzothiazole groups measured match the theoretical amount at low accelerator/sulfur ratios, but does not increase significantly with a corresponding increase in the amount of accelerator. Carbon-13 solid state NMR spectra were also collected for TBBS and BtSxBt [54]. These spectra contained only a broad resonance in the aromatic region under the experimental conditions used for measurement of the rubber samples. These results suggest that only an activated accelerator or similar species is being measured. This structure is an accelerator complex and not a rubber-bound intermediate as extraction causes the disappearance of this resonance as is illustrated in Figure 13. The exact nature of this structure has not been precisely determined.

There appears to be little dependence of the reaction products on either the amount of sulfur or accelerator present. Additionally, there does not appear to be a strong dependence of the reaction rate
of specific carbons on the amount of accelerator or sulfur present. The observable accelerator structure is probably the actual crosslinking species or a key intermediate to the reaction. Since this species reaches a maximum value, addition of further accelerator does not accelerate the reaction process. Thus the nature of the reaction products does not change with the amount of accelerator.

The amount of sulfurization in the sample varies directly with the amount of elemental sulfur in the formulation. This suggests that sulfur is consumed as needed by the accelerator complex; when the free sulfur is no longer available, then the reaction slows significantly. Further reaction from this point probably involves reduction in the sulfur content of the accelerator complex. This might explain why in Figure 7 the concentration of Alc (45 ppm) and Blc (58 ppm) reach a plateau at approximately 50-80 minutes cure and then increase at longer reaction times.

The percent of alpha carbons versus percent cure is shown in Figure 15. The curve rises quickly, and then increases linearly until full cure. Beyond this point the number of alpha carbons increases further, but the number of crosslinks decrease slightly. This may be due to desulfurization reactions, or may be due
to further reaction being predominantly intrachain, which would not result in a further increase in crosslink density. The sharp initial rise suggests that a steady-state value is reached for the rubber-bound intermediates.

Comparison of the molecular weight between crosslinks as measured by equilibrium swelling and as predicted by the NMR measurements is shown in Figure 16. The C-13 NMR curve parallels the equilibrium swelling curve initially, but the NMR curve predicts greater crosslink density during reversion while the equilibrium swelling curve illustrates reversion effects. Thus, we can conclude that at cure times greater than 60 minutes a significant percent of the sulfurization is related to non-crosslink structures.

Once the trans sulfurized structure appears in the sample it remains constant up to a cure of 300 minutes. The amount of trans sulfurization is shown as a function of cure time in Figure 17. Thus, the rate of reaction of this carbon relative to the other reacting carbons reaches an equilibrium quickly.

The mechanism of the reduction in sulfur rank is also of interest. There appears to be no migration or isomerization occurring adjacent to the site of
sulfurization. The mechanism of sulfur reduction must therefore be a concerted reaction involving cleavage of two sulfur bonds coupled with formation of either free sulfur or addition of the sulfur atoms to another structure. This mechanism also does not allow rotation into a single structure. Perhaps the reduction in sulfur rank is accompanied by an increase in the length of polysulfidic accelerator complexes. This could explain the simultaneous reduction of Alc and formation of polysulfidic Blc and Blt.

The fact that no cis-trans isomerization occurs indicates that the actual sulfurization proceeds through a single step mechanism. A stable intermediate is believed to be required for isomerization to occur in the elastomer. It is quite possible that if the loading levels were increased the nature of the reaction mechanism might change, and the sulfurization could proceed through a stable intermediate to allow isomerization.
V. CONCLUSIONS

Accelerated sulfur vulcanization of cis-polyisoprene by sulfur and tert-butyl benzothiazole sulfenamide results initially in the formation of a single polysulfidic structure. The initial structure is disulfidic in nature, and exhibits two distinguishable conformers. This structure then reduces in rank to a monosulfidic structure in a concerted fashion preserving the conformer ratio in the monosulfidic product. At longer cure times other polysulfidic structures form, which do not reduce in rank to monosulfidic products even at extremely long cure times. No reaction of the vinyl units, main chain scission, or double bond migration has been observed under these cure conditions with this accelerator.

The amount of sulfurization has been found to vary directly with elemental sulfur concentration, though the amount of accelerator or elemental sulfur does not affect the order or types of sulfurization products formed. The amount of trans sulfurized product is constant with cure time. NMR measurements provide reasonable estimates of equilibrium swelling values until the cure maximum is reached.
The benzothiazole groups observed do not exist in the form of a rubber-bound intermediate. The observable benzothiazole groups are most probably in the form of an activated accelerator, although the exact nature of this compound has not been determined. This structure is distinguishable from the accelerator and polysulfidic accelerator residues.
VI. ACKNOWLEDGEMENTS

We would like to acknowledge the Rubber Chemicals Division of Monsanto Corporation for their support of this research.
VII. REFERENCES


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34. Y. Tanaka, H. Sato, Polymer, 17, 113 (1976)


TABLE I
CIS-POLYISOPRENE FORMULATIONS

<table>
<thead>
<tr>
<th>Material</th>
<th>Formulation</th>
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<td></td>
<td>Conventional</td>
<td>Semi-Efficient</td>
<td>Efficient</td>
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<tr>
<td>Natsyn 2200</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
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<tr>
<td>Santocure NS</td>
<td>0.75</td>
<td>1.50</td>
<td>3.00</td>
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<td>Sulfur</td>
<td>2.38</td>
<td>1.50</td>
<td>1.08</td>
</tr>
<tr>
<td>Zinc Oxide</td>
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<td>5.00</td>
<td>5.00</td>
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<tr>
<td>Stearic Acid</td>
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TABLE II
T1 VALUES FOR POLYISOPRENE AT 300 MHZ

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<th>Cis T1 (ms)</th>
<th>Trans T1 (ms)</th>
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<tr>
<td>C1</td>
<td>137</td>
<td>191</td>
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<tr>
<td>C2</td>
<td>923</td>
<td>1294</td>
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<tr>
<td>C3</td>
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<td>274</td>
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<tr>
<td>C4</td>
<td>135</td>
<td>195</td>
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<tr>
<td>C5</td>
<td>774</td>
<td>1407</td>
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### TABLE III

**CHEMICAL SHIFT CALCULATIONS FOR ALPHA CARBONS IN CIS-POLYISOPRENE**

<table>
<thead>
<tr>
<th>Structure</th>
<th>Carbon</th>
<th>Mono</th>
<th>Poly</th>
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<tbody>
<tr>
<td>A1c</td>
<td>C4</td>
<td>50.6</td>
<td>42.8</td>
</tr>
<tr>
<td>B1c</td>
<td>C1</td>
<td>56.4</td>
<td>48.6</td>
</tr>
<tr>
<td>B1t</td>
<td>C1</td>
<td>64.8</td>
<td>57.0</td>
</tr>
<tr>
<td>A1c</td>
<td>C5</td>
<td>20.6</td>
<td>20.2</td>
</tr>
<tr>
<td>B1t</td>
<td>C5</td>
<td>13.6</td>
<td>13.2</td>
</tr>
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TABLE IV

CHEMICAL SHIFTS FOR ALPHA CARBONS OF POLYISOPRENE MODEL COMPOUNDS

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chemical Shifts (ppm)</th>
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<tbody>
<tr>
<td>A1S5S5A1</td>
<td>44.1</td>
</tr>
<tr>
<td>A1SSA1</td>
<td>44.0, 43.6</td>
</tr>
<tr>
<td>A1SA1</td>
<td>36.8</td>
</tr>
<tr>
<td>A1SSX</td>
<td>44.9</td>
</tr>
<tr>
<td>B1SSB1</td>
<td>48.9, 40.8</td>
</tr>
<tr>
<td>B1SB1</td>
<td>40.0</td>
</tr>
<tr>
<td>B1SSX</td>
<td>49.2</td>
</tr>
<tr>
<td>B1SX</td>
<td>42.9</td>
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</table>
Figure 1: Rheographs for the conventional, semi-efficient, and efficient formulations.
Figure 2: NMR spectrum of a sample from each formulation illustrating the dominant resonance of the cis-polyisoprene carbons.
Figure 3: List of possible structures occurring upon sulfurization of cis-polyisoprene.
Figure 4: NMR spectrum illustrating the new alpha carbon resonance at 51 ppm and the beta carbon resonance at 38 ppm.
Figure 5: NMR spectrum illustrating the new alpha carbon resonances at 64, 58 and 45 ppm.
Figure 6: NMR spectrum illustrating the new gamma carbon resonances at 17, 14 and 12 ppm.
Figure 7: Figure illustrating the change with cure of the peak at 51 ppm (Alc Polysulfidic).
Figure 8: Figure illustrating the change with cure of the peaks at 45 ppm (Alc Monosulfidic), 58 ppm (Blc Polysulfidic), and 64 ppm (Blt Polysulfidic).
Figure 9: Change in the peak at 14 ppm (Gamma carbon, Blt) plotted against the peak at 64 ppm (alpha carbon, Blt).
Figure 10: Change in the peaks at 12 and 17 ppm (Gamma carbon, B1c) plotted against the peak at 58 ppm (alpha carbon, B1c).
Figure 11: Structures of polyisoprene model compounds with nomenclature for each material. The measured chemical shifts for these structures [39] are listed in Table IV.
Figure 12: Change in trans, vinyl, and benzothiazole as a function of cure time for the conventional formulation.
Figure 13: NMR spectrum of extracted and unextracted sample of cis-polyisoprene illustrating the disappearance of the benzothiazole resonance.
Figure 14: Change in trans, vinyl, and benzothiazole as a function of accelerator/sulfur ratio.
Figure 15: The change in alpha carbons as a function of percent cure as measured by cure rheometry.
Figure 16: Figure comparing molecular weight between crosslinks for the conventional formulation as measured by equilibrium swelling and as predicted by NMR measurements.
Figure 17: Figure illustrating the percentage of trans sulfurization product as a function of cure time.
CHAPTER III

ANALYSIS OF THE MECHANISM OF TERT-BUTYL BENZOTHIAZOLE SULFENAMIDE ACCELERATED SULFUR VULCANIZATION OF CIS-POLYISOPRENE
I. INTRODUCTION

The relationship between chemistry and structure in network materials is of great interest in the polymer field. Understanding the correlation between these two factors is vital for development of new materials and optimization of existing compounds.

The relationship between chemistry and network structure is more complex for elastomers as opposed to typical thermosets. This arises from the complexity of vulcanization chemistry. Rubber accelerators do not react directly to form crosslinks; the accelerator reacts to form intermediates, which then react with the elastomer. Additionally, reactions of accelerator and sulfur with an elastomer do not necessarily result in crosslinks (intermolecular structures); cyclic formation (intramolecular structures) is also a significant reaction. These factors complicate the determination of the network structure for rubber, and require that several interrelating techniques be used for analysis.

There are several key questions that we sought to answer with this work: what is the role of zinc oxide? what is the relation between the chemistry and network structures?
The analysis of the vulcanization chemistry of the accelerator and the network structure of the elastomer has been published previously. This article will correlate the chemistry and structure formation, and include any additional experiments needed to help elucidate the vulcanization behavior of this system.

The investigation of the vulcanization chemistry, and specifically the fate of the accelerator, was conducted previously through the use of HPLC analysis [1] (Figures 1-3). The extra-network materials were extracted, and then measured and quantified by HPLC analysis. This work yielded results suggesting the behavior of the vulcanization system during the scorch delay and crosslinking elements during the vulcanization process.

The network structure had been measured during vulcanization through the use of solid-state C-13 NMR [2] (Figures 1, 4 and 5). These measurements were taken at varying degrees of cure to quantify the nature of the maturing network; emphasis was placed on measuring the network well into the reversion regime. The reversion process is very important in elastomers [3]; a better understanding of the changes in the network structure during the process is crucial to fully optimizing the properties of elastomers.
To aid and verify NMR peak assignments a solution polarization transfer experiment was performed. Elastomers are sufficiently mobile to allow such analysis by conventional solution techniques. The experiment used was the DEPT experiment (Distortionless Enhancement by Polarization Transfer), which allows determination of the number of bonded protons to a specific carbon.

Zinc oxide plays an important role in the vulcanization chemistry and the resulting network structure. To gain insight into the role of this activator, samples were analyzed in the presence and absence of zinc oxide and stearic acid. This allowed a better understanding of the role of zinc in the accelerator chemistry and network reactions.
II. EXPERIMENTAL

Accelerated-sulfur vulcanized samples of cis-polyisoprene were analyzed by several techniques. The HPLC analysis of the extra-network materials [1] and the C-13 NMR analysis [2] of the cured vulcanizate are described in detail in previous articles. NMR analysis was performed on a zinc-free conventional system; the methodology is identical to the previously published study [2]. NMR peak assignments were either confirmed or modified using the results of the chemical probe analysis and the results from the DEPT experiment, which provided information as to the number of protons attached to a given carbon. The three formulations analyzed are listed in Table I.

The DEPT sequence was performed at room temperature on a zinc-free sample cured to 100 percent cure. The recycle delay was 4 seconds, the spinning speed was 3.6 KHz, spectral frequency was 75.5 MHz, and 10,000 scans were collected.

Three samples were subjected to chemical probe analysis per the techniques of Cuneen and Russell [4]. These samples were cured for 36, 38 and 300 minutes, and were analyzed to determine if any crosslink structures were monosulfidic in nature [5].
Percent cure was measured by equilibrium swelling, correcting for chain ends and using the Moore-Watson calibration curve to correct for physical entanglements. Samples were swollen in n-decane, and the average of three consecutive days of constant measurements were used. The polymer-solvent interaction parameter $X$ is 0.43, the solvent molar volume in 194.90, the polymer molecular weight is 219,000, and the polymer density was 0.92.
III. RESULTS

Analysis of the chemistry of this accelerator system has been published previously [1], and was used for correlation with the C-13 solid-state NMR results. A1c/A2c polysulfidic structures formed only in the presence of BtSxBt complexes, while B1c and B1t polysulfidic structures formed in the presence of MBT and zinc salts of MBT. The amount of sulfurization was found to increase drastically in the absence of the zinc, but the resulting crosslink density was lower by a factor of 7. Zinc oxide did not influence the site of sulfurization. The samples cured for 36 and 38 minutes contained only polysulfidic structures, while the 300 minute sample contained some monosulfidic structures.
IV. DISCUSSION

A. NMR PEAK ASSIGNMENTS

For this spectroscopic work to contribute to the understanding of vulcanization chemistry the assignment of the NMR resonances must be well understood. Recently several papers have appeared analyzing the network structures of vulcanized natural rubber. These papers have both agreed and disagreed with our previous NMR peak assignments (Figures 1, 4 and 5) [6-7]. Thus, we reanalyzed our NMR assignments.

The peaks at 50.2 and 37 ppm have also been detected in other NMR studies of vulcanized natural rubber [6-7]. The consensus of the literature is that these peaks arise from an Alc polysulfidic structure. We previously attributed the peaks at 50.7 and 50.2 to a splitting of the Alc polysulfidic resonance due to distinguishable conformers; i.e., there exists two potential energy minima, and rotation between these states is slow relative to the NMR time scale. We used molecular modeling to test this conclusion. The results, shown in Figure 6, indicate that the minimum energy conformation occurs at approximately 90°. Thus, only one stable conformer exists; therefore, the source of this splitting is not distinguishable conformers.
Based on chemical probe studies [5], the peaks at 50.7, 50.2 and 37 ppm arise solely from polysulfidic structures. Attached proton test experiments in the literature and the DEPT experiment we performed indicated the peak at 50.7 ppm is a quaternary carbon. Based on these facts and chemical shift calculations, we have assigned the peak at 50.7 ppm to an A2c structure.

The peak at 58 ppm was found to be a methine structure by the DEPT experiment, which is consistent with a B1c polysulfidic structure. We also assigned the peak at 64 ppm to a B1t polysulfidic structure. We were unable to detect this structure in the DEPT experiment, but due to the low concentration of this structure it is possible that the signal intensity of this resonance was too low to be detected.

The peak at 45 ppm was assigned to a monosulfidic A1c structure in our past work. Recent NMR studies using the Attached Proton Test (APT) experiment have indicated that this resonance arises from a methylene group, which leads to the assignment of this peak to a C1c polysulfidic structure. However, it is also possible that the peak at 45 ppm consists of two overlapping bands. At low cure times (less than 40 minutes) the only sulfurization structures are A1c/A2c
polysulfidic structures, which disappear at longer cure times. We believe that the A-type structures reduce in sulfur rank to form monosulfidic structures with an NMR resonance at 45 ppm; sulfur rank reduction is a well-known phenomena in vulcanization [8]. Supporting evidence for this reduction in sulfur rank comes from the chemical probe work [5], which illustrates that there are monosulfidic crosslinks present at 300 minutes cure time. While the A1c/A2c peaks at 45 ppm would consist of methine and quaternary carbons, this does not necessarily contradict the DEPT and APT experimental data. If the concentration of C1c structures (methylene carbon) is significantly greater than the concentration of the A1c structures (methine carbon), then the peak would appear as a methylene. Additionally, it does not seem feasible that the A1c/A2c structures would undergo total migration and/or desulfurization. This would also explain the dual plateau in the plot of the peak at 45 ppm versus cure time shown in Figure 7. The initial rise is due to the conversion of the A-type polysulfidic structures to monosulfidic, while the latter rise is due to formation of new C1c polysulfidic structures.
B. HPLC/NMR CORRELATIONS

The HPLC data (Figures 2 and 3) illustrates that the intermediates BtSxBt \( (x=1-4) \) reach a maximum at approximately 20 minutes cure time, and then disappear at 40 minutes cure times. The accelerator TBBS disappears at 40 minutes cure time, and elemental sulfur is consumed by 60 minutes cure, which is when full cure is reached.

The solid-state C-13 NMR results have found a limited number of sulfurization structures, shown in Figures 4 and 5. At low cure times the sole sulfurization structures are polysulfidic A1c/A2c. After 40 minutes cure time the A1c/A2c polysulfidic structures reduces in sulfur rank to monosulfidic, and new structures B1c and B1t polysulfidic are formed. As the cure time is increased into the reversion regime (greater than 70 minutes cure) new C1c structures are formed. The dominant structures after significant reversion are the B1c and C1c structures.

A direct comparison between the chemistry analysis in Figures 2 and 3 and network measurements in Figures 4 and 5 leads to several interesting observations. The A1c/A2c structures are formed only in the presence of BtSxBt compounds; this leads to the conclusion that the
reaction for formation of AlcSxBt (or A2cSxBt) is:

\[
\text{Rubber} \quad \xrightarrow{\text{BtSxBt}} \quad \text{Alc-SxBt + MBT} \quad (1)
\]

At longer cure times (40 minutes and greater), no new BtSxBt is formed. According to the HPLC data, from 40 to 70 minutes all of the benzothiazole groups are in the form of MBT. This is misleading, as zinc complexes of MBT will be measured as MBT due to the nature of the HPLC sampling process. As mentioned previously, the time period between 40 and 70 minutes is when the Blc and Blt structures are formed. This leads to the hypothesis that the Blc and Blt structures form via Reaction (2):

\[
\text{BtSxZnSxBt + Rubber} \quad \xrightarrow{\text{}} \quad \text{BlSxBt + MBT + Zn} \quad (2)
\]

This would also agree with the work of Campbell and Wise [9]. Their work involved HPLC analysis of vulcanization as presented here, but additionally, they also followed the change in the ZnMBT and soluble zinc as a function of cure. Their work found that the concentration of zinc complexes rose shortly after initiation of cure, and reached a maximum near full cure for a sulfenamide system.
The nature of the reaction mechanisms changes upon consumption of elemental sulfur. At cure times greater than maximum cure the amount of sulfurization increases dramatically, yet the extent of crosslinking decreases by 15 percent for 300 minutes cure as shown in Table II. The sulfur for continued sulfurization is obtained through reduction in sulfur rank of the polysulfidic crosslinks. What is interesting to note is that sulfur obtained via this route does not increase the extent of crosslinking. A probable reaction scheme for this is:

\[ \text{B1c-Sx-B1c (xlink)} + \text{MBTZnMBT} \rightarrow \text{B1c-S(x-y)-B1c (cyclic)} + \text{MBTSxZnSxMBT} \] (3)

This converts crosslinked structures to cyclic structures, and also provides further accelerator complexes for sulfurization. This would also account for the reduction in crosslinking; if the reformed complex then forms a cyclic structure there is a net reduction in the number of crosslinks. This reaction scheme also allows for conversion of cyclics to crosslinks, and also reduction in rank of crosslinks and cyclic structures. It should be noted that this scheme, while drawn for B1c structures, can be applied to any network structure.
It is also important to note that the Clc structures do not form until the reversion regime. Another possible reversion scheme is that the Clc structures are formed by migration of the site of sulfurization in Reaction (3); instead of a single step reaction as is illustrated, the reaction forms an intermediate, which then reacts as in:

\[
\text{Blc-Sx-Blc (xlink)} + \text{MBTZnMBT} \rightarrow \text{Blc-S(x-y)-Bt + MBTSxZnSxMBT (4)}
\]

\[
\text{Blc-S(x-y)-Bt + Isoprene} \rightarrow \text{Blc-S(x-y)-Clc (5)}
\]

It should also be noted that since the formation of Clc polysulfidic structures occurs during the reversion period, these structures will be predominantly cyclic in nature.

The effect of the accelerator and sulfur content on the sulfurization and crosslinking are fairly straightforward. As the sulfur content is decreased, the amount of sulfurization is reduced; this was reported previously [2]. This is obvious by the reactions discussed previously; the sulfurization reduction is dependent on elemental and combined sulfur. The accelerator plays an important role in the efficiency of crosslinking. The greater the accelerator concentration, the higher the percentage of
crosslinks per sulfurization. This may also be dependent on the sulfur rank of the accelerator complex; shorter polysulfidic complexes may react in a more efficient manner.

This mechanism is supported by the work of Layer [10-11], which involved taking elastomers at full cure and swelling in additional sulfur [10] or additional accelerator [11]. Layer concluded that exchange reactions play a key role in the vulcanization chemistry.

To help understand the role of zinc in the vulcanization chemistry, the conventional formulation was analyzed in the presence and absence of zinc to determine the role of zinc in the vulcanization chemistry. The results, shown in Table II, contain several key points. The most significant conclusion is that the amount of sulfurization at maximum cure is increased in the zinc-free system by more than a factor of 4. Additionally, the type and distribution of crosslink products does not vary between the zinc-free and zinc-containing systems. The zinc-free and conventional formulation contain the same percentage of B1 structures; however, the ratio of B1t to total B1 structures decreases in the zinc-free system. The amount of sulfurized carbons stands in stark contrast
to the equilibrium swelling values; the degree of crosslinking is lower by a factor of 7 for the no-zinc system, indicating formation of cyclics dominates over crosslink formation.

This data leads to several conclusions about the role of zinc in TBBS-accelerated sulfur vulcanization. Zinc is intimately involved the crosslinking reaction:

\[ \text{AlcSxBt} + \text{Zn} + \text{Isoprene} \rightarrow \text{AlcSxAlc} + \text{Zn} + \text{MBT} \] (6)

In the absence of zinc the crosslinking reaction still occurs but much less efficiently. The change in the cis/trans distribution of the B-type structures suggests that zinc plays a role here; the B1 structures are formed in a given cis/trans ratio during the crosslinking/cyclization step, and the removal of zinc changes the equilibrium values.

Figure 8 illustrates the relationship between percent cure and percent sulfurization. Up to 0.30-0.35 percent sulfurization, there is a fairly linear relationship. Beyond this point, the percent sulfurization continues to increase while the percent cure decreases. This is due to the exchange reactions discussed earlier converting crosslink structures to cyclic structures, while simultaneously reforming the active accelerator complex.
There are several interesting comparisons that can be made between the chemistry of this system and systems analyzed in the literature. A significant portion of the rubber literature has been devoted to determining whether vulcanization occurs via polar, radical or combination mechanisms. Among the more notable work in this area is the work of Manik and Banerjee [12]. Their work analyzed natural rubber cured with cyclohexyl benzothiazole sulfenamide (CBS) and sulfur in the presence and absence of zinc oxide and stearic acid. CBS is chemically very similar to TBBS; the sole difference is the exact alkyl group contained in the sulfenamide. Their conclusions, which are listed in Table III, found that for CBS in the presence of zinc oxide and stearic acid initial crosslinking was radical but during the main crosslinking period the reaction was polar. In the absence of zinc oxide and stearic acid the reaction was found to be completely radical. In this system the initial crosslinking reaction has been shown to be different than the main crosslinking reaction. It is possible that the BtSxBt complexes react through a radical sulfurization process, and that the zinc salt complexes react through a polar sulfurization process.
The work of Shelton and McDonel provides further evidence for this possibility [13]. Their work used radical scavengers and equilibrium swelling measurements to determine whether a given formulation was polar or radical. Their conclusion was that sulfenamide-sulfur systems were mixed radical and polar. Similar conclusions were reached by Morita and Young on a variety of sulfenamides including TBBS [14]. Their work concluded that both radical and polar processes were occurring in sulfenamide vulcanization. It should be noted that all of the formulations in the work of Morita and Young and Shelton and McDonel included zinc oxide and stearic acid in the formulations.
V. CONCLUSIONS

Accelerated sulfur vulcanization in the presence of zinc proceeds through two reactive intermediates, BtSxBt and BtSyZnSyBt. The A1c/A2c structures are formed through BtSxBt intermediates, while zinc salt intermediates are responsible for formation of the B1c/B1t structures. C1c structures form only during the reversion process, and most probably arise from migration of B1 structures during the reversion reaction. A1c/A2c structures are formed only during the initial vulcanization steps, while B1c and B1t structures are formed continuously during the main crosslinking period and throughout the remainder of the curing process. Several reactions were proposed to account for the change in structures during the cure and reversion regimes.
VI. REFERENCES


5. Shirley Lee, Monsanto Chemical Company, Rubber Chemicals and Process Division, Unpublished Results


7. R.C. Hirst, Presented at Rubber Division Meeting, Detroit, Michigan, Paper No. 69, October 1991


**TABLE I**

**CIS–POLYISOPRENE FORMULATIONS**

<table>
<thead>
<tr>
<th>Material</th>
<th>Conv.</th>
<th>SEV</th>
<th>EV</th>
<th>Conv. Zinc-Free</th>
</tr>
</thead>
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<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
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<td>1.50</td>
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</tr>
<tr>
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<td>1.50</td>
<td>1.08</td>
<td>2.38</td>
</tr>
<tr>
<td>Zinc Oxide</td>
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<td>5.00</td>
<td>5.00</td>
<td>-</td>
</tr>
<tr>
<td>Stearic Acid</td>
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<td>3.00</td>
<td>3.00</td>
<td>-</td>
</tr>
<tr>
<td>%Cure</td>
<td>%Sulf.</td>
<td>%Bl/ Sulf.</td>
<td>%Blt/ Bl</td>
<td>Mc</td>
</tr>
<tr>
<td>-------</td>
<td>--------</td>
<td>------------</td>
<td>----------</td>
<td>-----</td>
</tr>
<tr>
<td>92.1</td>
<td>0.253</td>
<td>45.5</td>
<td>31.3</td>
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</tr>
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<td>28.3</td>
<td>5747</td>
</tr>
<tr>
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<td>26.3</td>
<td>5747</td>
</tr>
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<td>78.6</td>
<td>0.793</td>
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<td>33.0</td>
<td>7017</td>
</tr>
</tbody>
</table>

Conventional (zinc-free)

<table>
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<th>%Cure</th>
<th>%Sulf.</th>
<th>%Bl/ Sulf.</th>
<th>%Blt/ Bl</th>
<th>Mc</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.993</td>
<td>37.8</td>
<td>8.3</td>
<td>38220</td>
</tr>
<tr>
<td>100.0</td>
<td>1.195</td>
<td>39.2</td>
<td>7.5</td>
<td>38160</td>
</tr>
<tr>
<td>Formulation</td>
<td>Results</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>--------------------------</td>
<td>------------------------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NR-CBS-S</td>
<td>Radical</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NR-S-ZnO-CBS-Stearic Acid</td>
<td>Radical initiation Polar during main crosslinking</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NR-MBT-S</td>
<td>Radical</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 1: Chemical structures measured using NMR and HPLC measurements.
Figure 2: HPLC data of extra-network materials in conventional formulations. Taken from Reference 1.
Figure 3: HPLC data of extra-network materials in conventional formulations. Taken from Reference 1.
Figure 4: Figure illustrating the change in amount of A1c/A2c polysulfidic structures as a function of cure time. Data taken from Reference 2.
Figure 5: Figure illustrating the change in amount of peaks at 58, 64 and 45 ppm as a function of cure time. Data taken from Reference 2.
Figure 6: Plot of conformational energy of AlcSSAlc molecule as function of rotation angle of C-S-S-C structure.
Figure 7: Plot of peak at 45 ppm versus cure time. Data taken from Reference 2.
Figure 8: Plot of percent sulfurized carbons for the conventional system versus percent cure.
CHAPTER IV

SOLID STATE CARBON-13 NMR STUDIES OF TERT-BUTYL BENZOTHIAZOLE SULFENIMIDE (TBSI) ACCELERATED SULFUR VULCANIZATION OF CIS-POLYISOPRENE
I. INTRODUCTION

Optimization of network properties requires a knowledge of the network structures and chemistry of network formation [1-2]. Tables I and II provide insight into the importance of understanding the network structure. These tables relate a variety of network structures to a wide range of mechanical and physical properties [1]. Ultimately, the formulator would like to be able to choose formulations based on a fundamental knowledge of the network structure and the chemistry that leads to specific structures. To date, there is not a complete and comprehensive understanding of the relationship between network structure and chemistry.

Accelerated sulfur vulcanization of elastomers has been studied by NMR analysis in many previous works [3-19]. Improvements in NMR technology now permit analysis of vulcanized elastomers at the low curative levels that are commercially used. Much of this recent work has concentrated on cis-polyisoprene and natural rubber due to the widespread use of these elastomers industrially [3-11].
Previous work in our laboratories had analyzed the network structure of cured polyisoprenes [3-7]. One previous study involved analysis of the network resulting from sulfur vulcanization accelerated by tert-butyl benzothiazole sulfenamide (TBBS) [3]. These two accelerators, shown in Figure 1, are chemically very similar, which allows us to probe more precisely the role of the accelerator in network formation. The goal of this study is to analyze the network structure of TBSI accelerated vulcanizates and correlate the network structure with accelerator chemistry. Additionally, we will compare the network structures observed in TBSI and TBBS accelerated systems.

Also contributing strongly to the understanding of the sulfenamide accelerators is the HPLC analysis of the extra-network materials [20-21]. The chemistry of the accelerator complexes coupled with the knowledge of the network structure has shown to be a powerful tool in elucidating the relationship between chemistry and structure [4].
II. EXPERIMENTAL

All samples for this study were supplied by the Rubber Chemicals and Process Division of Monsanto Chemical Company. A Monsanto oscillating disc rheometer (ODR) was modified so as to include several small disks on the outer edge of the rheometer mold. These disks were of the proper diameter to be used in a 7 mm zirconia rotor for analysis for solid-state NMR. This mold ensured that the exact extent of cure for the samples would be known, as the extent of cure was measured simultaneously with sample preparation.

Samples were cured for times ranging from 50 minutes to 300 minutes for the conventional system and from 60 minutes to 300 minutes for the semi-efficient and efficient systems. The formulations are listed in Table III, and the rheometer traces for each formulation are shown in Figure 2. The conventional system was analyzed for a greater number of cure times to determine the sulfurization products for this system. These results were then used to analyze the spectra from the semi-efficient and efficient vulcanization systems. Samples were cured at 140°C.
All NMR measurements were performed on a Bruker MSL 300 at a carbon frequency of 75.47 MHz. Measurements were performed at room temperature on a CP/MAS probe using magic angle sample spinning and gated high power decoupling. Quantitative measurements were performed using 8000 scans and a recycle delay of 8 seconds, while for non-quantitative measurements a recycle delay of 2 seconds was used and 30000 transients were collected. The data was transferred from the MSL 300 to a Microvax III+ using Ethernet, where the data was analyzed using in-house software developed in FORTRAN 77.

Quantitative measurements in C-13 NMR require that the recycle delay be longer than 5 times the longest T1 spin-lattice relaxation time. T1 values were measured for the cis-polyisoprene and trans-polyisoprene carbons in a previous study [3]; at a delay time of 8 seconds the cis and trans-polyisoprene are fully quantitative. The assumption was made that the vinyl carbons would show similar T1 relaxation behavior to the cis and trans carbons.

Assignment of NMR peaks was performed using previously published work [3-4]. This work includes analysis of the number of bonded protons through the DEPT experiment and calculation of chemical shifts of
sulfurization structures through use of chemical shift additivity constants based on model compounds.

Equilibrium swelling measurements were performed using n-decane as a solvent. Samples were weighed until several successive measurements illustrated equilibrium had been reached. The polymer-solvent interaction parameter is 0.43, and the molecular weight of the uncured rubber is 219,000. The density of the rubber was taken as 0.93 g/cc, while the solvent molar volume is 194.90. The Moore-Watson calibration curve for chain entanglements was used.
III. RESULTS

Several new resonances were detected in all three formulations upon vulcanization. New resonances at 50.7, 50.2 and 37 ppm were detected at low cure times (Figure 3). At longer cure times these resonances disappeared and new resonances were detected at 58, 64 and 45 ppm (Figure 4), along with new peaks at 17, 14 and 12 ppm (Figure 5). Similar results were found for all three formulations, but the level of sulfurization decreased from conventional to semi-efficient to efficient formulations, even though the crosslink density at full cure was similar for all systems.

In the semi-efficient system at long cure time a new peak was observed at 50 ppm in the 100 minute cure sample (Figure 6). This peak was not seen in the conventional formulation, and the S/N ratio was too low in the efficient system to observe this resonance.

No evidence was seen for main chain scission. A slight amount of cis/trans isomerization was observed, which increased with increasing sulfur content. Reversion of TBSI was found to exhibit a lower degree of continued sulfurization as opposed to TBBS samples. Based on equilibrium swelling measurements, TBSI was found to be a less efficient accelerator than TBBS.
IV. DISCUSSION

A. TBSI NMR RESULTS

Analysis of the chemical microstructure was carried out using C-13 solid-state NMR. The first, most noticeable, result was the effect of sulfur content on the overall level of sulfurization. As the concentration of sulfur in the formulation was decreased, the level of sulfurization decreased significantly. Thus, the concentration of sulfurized carbons is directly related to the sulfur content.

At low cure times new resonances are measured at 50.7, 50.2 and 37 ppm as seen in Figure 3. The peaks at 50.2 and 37 ppm have been previously assigned to the polysulfidic structure Alc (Figure 1) [3-4], while the resonance at 50.7 ppm arises from a polysulfidic A2c structure [4]. These resonances are the only new peaks at 50 minutes cure, and disappear almost completely by 60 minutes cure.

At longer cure times we detected several new sulfurization resonances at 45, 58, 64 and 50 ppm (Figures 4 and 6). The resonance at 45 ppm was assigned to the monosulfidic Alc and A2c structures, and polysulfidic Clc structure (Figure 1). The
assignment of the peaks at 64 and 58 ppm was to Blt and B1c polysulfidic structures (Figure 1). The peak at 50 ppm at longer cure times was assigned to a monosulfidic B1c structure. This peak appeared in the semi-efficient system, but did not appear consistently with longer cure times. We believe that this arises from nonuniformity of cure with low sulfur levels in the formulation. The peaks at 17 and 12 ppm (Figure 5) were assigned to the methyl carbons in a B1c polysulfidic structure, while the peak at 14 ppm (Figure 5) was assigned to a Blt polysulfidic structure.

There has been some disagreement in the literature as to the exact nature of the peaks at 50.7, 50.2, 45 and 64 ppm. Our previous work [3-4] discusses these assignments in greater detail.
B. COMPARISON OF TBBS AND TBSI FORMULATIONS

The overall type and relative distribution of products with TBSI are similar to those found with TBBS accelerated systems. Comparisons of the amount of B1 structures at full cure in the TBBS and TBSI systems are shown in Table IV. The percentage of B1 crosslinks in the system is comparable between the two accelerators. It is interesting to note that the amount of sulfurization at full cure is greater in the TBSI system than in the TBBS system, yet the level of crosslinking is very similar. Another point to note is that the amount of sulfurization that occurs after full cure is reached is significantly lower in the TBSI system then in the TBBS system.

A significant advantage of the NMR and HPLC analysis of the vulcanized systems is that it allows calculation of the average length of sulfurized chains in the elastomer. HPLC data showed complete consumption of elemental sulfur and absence of BtSxBt structures at full cure. Thus, we can conclude that at full cure the elemental sulfur originally added is contained almost exclusively in network structures. If we assume only polysulfidic structures, then the value of RSxR for the TBBS conventional system is 8.0, while
for the TBSI conventional system the value is 4.8. The details of these calculations are discussed in Appendix I. Thus, TBSI produces more and shorter sulfurization structures as compared to TBBS accelerated systems. This behavior is also related to the lower degree of reversion; the TBSI systems undergoes less reaction in the reversion regime then TBBS systems due to shorter chains. This is due to the reversion reaction being of the nature [4]:

\[ \text{Blc-Sx-Blc (xlink) + MBTznMBT} \rightarrow \text{Blc-S(x-y)-Blc (cyclic) + MBTSxZnSxMBT} \] (1)

The reversion reaction may also be a two-step reaction:

\[ \text{Blc-Sx-Blc (xlink) + MBTznMBT} \rightarrow \text{Blc-S(x-y)-Bt MBTSxZnSxMBT} \] (2)

\[ \text{Blc-S(x-y)-Bt + Isoprene} \rightarrow \text{Blc-S(x-y)-C1c} \] (3)

The shorter TBSI chains have a lower reactivity; thus TBSI exhibits greater reversion resistance. These reactions are shown for the Blc and C1c polysulfidic structures, but are applicable to any polysulfidic structure. The HPLC data illustrates that the benzothiazole groups are in the form of MBT and/or the zinc salts of MBT during the reversion process. Thus,
reversion reactions occur through the zinc-sulfur-benzothiazole complexes [4].

The appearance of the monosulfidic B1c structure in the semi-efficient system provides further insight into the nature of the reversion process. The reversion product of polysulfidic Clc suggests that Reactions (2) and (3) occur significantly, but the reversion product of B1c monosulfidic could result from either Reaction (1) or Reactions (2) and (3).

Equilibrium swelling measurements lead to an interesting conclusion. At full cure in the TBSI samples there is 0.42% sulfurization to obtain a Mc (molecular weight between crosslinks) of 5100, yet for the TBBS samples only 0.25% sulfurization is required to obtain an Mc of 5800. The large difference in sulfurization to achieve similar levels of crosslinking indicates in a TBSI formulation a greater percentage of structures are cyclic in nature as compared to the TBBS formulations. However, these structures are more stable with increased cure time as mentioned previously.

Table V illustrates the change in the unreacted trans and vinyl isomers as a function of accelerator/sulfur ratio. As the sulfur concentration
is increased, the amount of isomerization increases, but the overall level of isomerization is still quite small. This is similar to the TBBS results [3], which showed no isomerization, but vastly different from previous vulcanization studies [5-7, 9, 13-19, 22, 23], which exhibited large levels of isomerization.
V. CONCLUSIONS

TBBSI accelerated sulfur vulcanization results in several new sulfurization structures. At low cure times only a A1c and A2c polysulfidic structures are observed. At longer cure times the A1c and A2c polysulfidic structures reduces in sulfur rank to monosulfidic, and B1c, B1t and Clc polysulfidic structures are observed. B1c monosulfidic resonance was observed in a semi-efficient sample.

TBBS accelerated sulfur vulcanization was found to produce a greater crosslink/cyclic ratio than TBSSI accelerated vulcanization, but was also found to undergo greater reversion than TBSSI samples. This was related to the longer sulfurization chains at full cure for TBBS conventional samples as opposed to TBSSI conventional samples. A slight amount of isomerization was found to occur, which decreased with decreasing sulfur content.
VI. ACKNOWLEDGEMENTS

The authors would like to acknowledge the support of the Rubber Chemicals and Process Division of Monsanto Chemical Company for their support of this research, and for allowing use of the HPLC data in connection with this paper.
VII. REFERENCES


9. R.C. Hirst, Rubber Division Meeting, Detroit, Michigan, October 1991, Paper No. 69


<table>
<thead>
<tr>
<th>Property</th>
<th>Change with increase in proportion of di- and polysulfides</th>
</tr>
</thead>
<tbody>
<tr>
<td>creep, stress relaxation</td>
<td>increase</td>
</tr>
<tr>
<td>set</td>
<td>increase</td>
</tr>
<tr>
<td>incremental swelling</td>
<td>increase</td>
</tr>
<tr>
<td>tensile strength, tear strength</td>
<td>increase</td>
</tr>
<tr>
<td>resilience</td>
<td>increase</td>
</tr>
<tr>
<td>fatigue failure</td>
<td>decrease</td>
</tr>
<tr>
<td>heat resistance</td>
<td>decrease</td>
</tr>
<tr>
<td>thermal aging resistance</td>
<td>decrease</td>
</tr>
</tbody>
</table>

Taken from Reference 1.
**TABLE II**

**INFLUENCE OF MAIN-CHAIN MODIFICATIONS ON PROPERTIES**

<table>
<thead>
<tr>
<th>Property</th>
<th>Change with increase in degree of modification</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Olefinic*</td>
</tr>
<tr>
<td>resilience</td>
<td>decrease</td>
</tr>
<tr>
<td>strength*</td>
<td>decrease</td>
</tr>
<tr>
<td>fatigue failure</td>
<td>decrease?</td>
</tr>
<tr>
<td>swelling in hydrocarbon</td>
<td>decrease?</td>
</tr>
<tr>
<td>oils</td>
<td></td>
</tr>
<tr>
<td>oxidative aging resistance</td>
<td>decrease</td>
</tr>
<tr>
<td>low-temperature crystallization</td>
<td>rate decrease</td>
</tr>
</tbody>
</table>

*Includes conjugated diene and triene groups and cis, trans-isomerized units.

*Especially high-temperature strength.

Taken from Reference 1.
<table>
<thead>
<tr>
<th>Material</th>
<th>Conv.</th>
<th>SEV</th>
<th>EV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cis-polyisoprene (Natsyn 2200)</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td>TBSI (Santocure TBSI)</td>
<td>0.75</td>
<td>1.50</td>
<td>3.00</td>
</tr>
<tr>
<td>Sulfur</td>
<td>2.38</td>
<td>1.50</td>
<td>1.08</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>5.00</td>
<td>5.00</td>
<td>5.00</td>
</tr>
<tr>
<td>Stearic Acid</td>
<td>3.00</td>
<td>3.00</td>
<td>3.00</td>
</tr>
</tbody>
</table>
TABLE IV

COMPARISON OF TBSI AND TBBS VULCANIZATION FOR CONVENTIONAL FORMULATIONS

<table>
<thead>
<tr>
<th>%Cure</th>
<th>Acc.</th>
<th>Cure Time</th>
<th>%Sulf.</th>
<th>Mc</th>
<th>%Bl/ Sulf.</th>
</tr>
</thead>
<tbody>
<tr>
<td>92.8</td>
<td>TBSI</td>
<td>80</td>
<td>0.426</td>
<td>5503</td>
<td>47.7</td>
</tr>
<tr>
<td>99.3</td>
<td>TBSI</td>
<td>90</td>
<td>0.418</td>
<td>5087</td>
<td>47.4</td>
</tr>
<tr>
<td>95.4</td>
<td>TBSI</td>
<td>100</td>
<td>0.475</td>
<td>5156</td>
<td>45.9</td>
</tr>
<tr>
<td>----</td>
<td>TBSI</td>
<td>300</td>
<td>0.668</td>
<td>5756</td>
<td>40.3</td>
</tr>
<tr>
<td>96.1</td>
<td>TBBS</td>
<td>55</td>
<td>0.254</td>
<td>5800</td>
<td>45.3</td>
</tr>
<tr>
<td>100.0</td>
<td>TBBS</td>
<td>60</td>
<td>0.253</td>
<td>5988</td>
<td>45.5</td>
</tr>
<tr>
<td>95.0</td>
<td>TBBS</td>
<td>70</td>
<td>0.315</td>
<td>5747</td>
<td>51.4</td>
</tr>
<tr>
<td>83.1</td>
<td>TBBS</td>
<td>300</td>
<td>0.793</td>
<td>7016</td>
<td>42.7</td>
</tr>
<tr>
<td>System</td>
<td>% Trans</td>
<td>% Vinyl</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----------------------</td>
<td>---------</td>
<td>---------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conventional</td>
<td>1.62 ± 0.0</td>
<td>0.38 ± 0.03</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Semi-Efficient</td>
<td>1.50 ± 0.07</td>
<td>0.43 ± 0.08</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Efficient</td>
<td>1.3 ± 0.1</td>
<td>0.34 ± 0.08</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cis-Polyisoprene (Natsyn 2200)</td>
<td>1.4</td>
<td>0.40</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 1: Chemical structures of accelerators and observed network structures in TBSI accelerated vulcanization.
Figure 2: Rheographs for the three formulations studied in this work.
Figure 3: C-13 NMR spectrum illustrating new resonances at 50.7, 50.2 and 37 ppm.
Figure 4: C-13 NMR spectrum illustrating new peaks at 64, 58 and 45 ppm.
Figure 5: C-13 NMR spectrum illustrating new resonances at 17, 14 and 12 ppm.
Figure 6: C-13 NMR spectrum illustrating new resonance at 50 ppm.
APPENDIX I

CALCULATION OF X IN RSxR

The calculation of the length of the sulfur chain between sites of attachment is a value that has been used in evaluating the efficiency of vulcanization systems for many years [22]. The HPLC data [21] illustrates that all elemental sulfur is consumed into network structures, as it is not present as BtSxBt at full cure nor is it present as elemental sulfur. From this, it is possible to measure a value for x.

The measurement of x at full cure is calculated as follows: in the conventional formulation there is 100 phr of rubber and 2.38 phr of sulfur. We need to convert these values to moles of carbon and sulfur. For carbon:

\[
100 \text{ g Rubber} \times \frac{60.01 \text{ g C}}{58.12 \text{ g/mole}} = 88.16 \text{ g C}
\]

\[
88.16 \text{ g C} \times \frac{1 \text{ mole}}{12.01 \text{ g}} = 7.34 \text{ moles C}
\]

For sulfur:

\[
2.38 \text{ g S} \times \frac{1 \text{ mole}}{32.06 \text{ g}} = 7.42 \times 10^{-2} \text{ moles S}
\]
This gives us the total number of moles of carbon and sulfur. From the NMR data we know the percentage of carbon that has bonded sulfur. From these percentages and the total number of moles of carbon we can calculate moles of sulfurized carbon. The moles of sulfur divided by moles of sulfurized carbon times 2 gives the value of \( x \), which is shown in Table I. The factor of 2 arises from the fact that for any network structure other than rubber-bound intermediates there is a carbon on each end of the sulfur chain.

This calculation assumes only polysulfidic structures, which we know is not completely accurate. Additionally, it does not account for any loss of sulfur, such as in the form on ZnS. Still, this gives a qualitative feel for the length of sulfur chains in these vulcanizates.
<table>
<thead>
<tr>
<th></th>
<th>TBSI</th>
<th>TBBS</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Sulfurization</td>
<td>0.426</td>
<td>0.254</td>
</tr>
<tr>
<td>at Full Cure</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moles</td>
<td>3.13</td>
<td>1.86</td>
</tr>
<tr>
<td>Sulfurization x 10^2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>X value</td>
<td>4.7</td>
<td>8.0</td>
</tr>
</tbody>
</table>
CHAPTER V

SPIN–SPIN MOTIONAL ANALYSIS OF ACCELERATED SULFUR VULCANIZED CIS–POLYISOPRENE
I. INTRODUCTION

The use of proton NMR to analyze the motional behavior of elastomeric systems has shown increased utility in recent years. There are a wide variety of experiments to probe a range of motional frequencies, and consequently, different motional behaviors. Analysis of elastomeric systems has shown wide use of spin-spin (T2) relaxation measurements. T2 measurements probe the kilohertz motional regime, which is the frequency range of longer range cooperative motions. These motions are highly affected by crosslinking reactions and the dispersion of the network junction points. Applications of T2 measurements to elastomers have included analysis of dispersion of carbon black in rubber [1-2], real-time measurement of solvent diffusion into elastomers [3], analysis of crosslinked elastomers [4-10], measurement of T2 behavior as a function of temperature [11], analysis of domain size in blends [12], spatial analysis of swollen vulcanizates [13], and analysis of degradation mechanisms [14]. Thus, this technique is an ideal method for analysis of accelerated sulfur vulcanizates. The main goal of this study is to quantify the relationship between the sulfurization and
crosslinking processes and the change in T2 parameters.

We studied three formulations with different accelerator/sulfur ratios. This allows us to separate the effects of sulfurization and crosslinking. All three series of samples are of similar crosslink density, but contain varying amounts of sulfurization. These samples have been previously analyzed by solid-state C-13 NMR to quantify the types and amounts of sulfurization structures [15-16].

Previous work in the literature has found that the T2 relaxation process in many elastomers is not a simple exponential decay, but exhibits biexponential or more complicated behavior [1-6,8-14]. The non-exponential behavior is seen only in the solid-state [1,4,9,11,12]. The two component biexponential decays have been attributed to mobile regions (chain segments distant from crosslinks) and to crosslink regions. In several cases the decay exhibits non-exponential decay in addition to biexponential behavior [4,9,12]. The non-exponential behavior occurs when the material is below the glass transition temperature [9,11,12] or tightly bonded to a material below its Tg [1]. An exception to this is the behavior of polybutadiene, which exhibits mixed relaxation behavior (predominantly Lorenztian) above Tg [11].
Alternatively, non-exponential decay arises from residual anisotropic motions related to crosslink structures which are not motionally averaged to zero [4].

The swollen samples in this study exhibited very little non-exponential behavior. Thus, we used the approximation that solvating of the elastomers effectively reduces the residual anisotropic motions to zero. This is not rigorously true, and is thus only an approximation; most of the samples studied exhibited very small amounts of gaussian decay behavior.

Solid-state C-13 NMR studies performed previously were used to correlate the relaxation behavior with amount of sulfurization. NMR can measure carbons with directly-bonded sulfur (sulfurization), but cannot distinguish between cyclic (intramolecular) and crosslink (intermolecular) structures. Thus, we will discuss vulcanization in terms of amount of sulfurization as opposed to amount of crosslink formation.

Many previous works in the literature have been concerned with physical versus chemical crosslinks, and how the physical crosslinks affect the motional behavior. To separate out the chemical crosslinks from
the physical crosslinks, the percent cure was measured by equilibrium swelling and the physical crosslinks subtracted via the use of the Moore–Watson calibration curve [17]. This correction allows the determination of only chemical crosslinks from the "total" number of crosslinks. Thus, our graphs reflect only chemical crosslinks.
II. EXPERIMENTAL

The NMR experiments were run on a Bruker MSL 300 using a micro-imaging probe with the gradients disconnected. This method allowed analysis of swollen rubber disks that had been previously analyzed by high resolution C-13 solid-state NMR. Spin-spin (T2) relaxation values were measured at room temperature using the Carr-Purcell spin-echo sequence shown in Figure 1. The spectral frequency was 300.13 MHz, the spectral width was 7500 Hz, and a recycle delay of 3 seconds was used. For each echo time 120 scans was collected, resulting in a total experimental times of approximately 3 1/2 hours. The spectral endpoints were set using a previous literature value of 5.1 ppm for the olefinic proton resonance [16].

The cis-polyisoprene formulations analyzed are shown in Table I. Samples were cured for times ranging from 30 minutes to 180 minutes for the conventional system (Formulation 2B) and from 42 minutes to 105 minutes for the semi-efficient and efficient systems (Formulations 3B and 4B). The oscillating disc (ODR) rheometer traces for each formulation are shown in Figure 2. Samples were cured at 140°C.
All samples for this study were supplied by the Rubber Chemicals and Process Division of Monsanto Corporation. The samples were prepared in a Monsanto oscillating disc rheometer which was modified to include several small disks on the outer edge of the rheometer mold. These disks were of the proper diameter to be used in a 7 mm zirconia rotor for analysis by solid-state NMR. This mold ensured that the samples could be analyzed by solid-state C-13 NMR and then subsequently by proton NMR relaxation measurements.

Equilibrium swelling measurements were used for percent cure measurements to account for any cure rate differences between the center of the ODR mold and the outer edge, where the disks were prepared. Swelling measurements were performed using n-decane as a solvent. The molecular weight of the uncured sample was 219,000 and the polymer-solvent interaction parameter used was 0.43. The density of the rubber was taken as 0.93 g/cc, and the solvent molar volume used was 194.90. The Moore-Watson calibration curve was used to correct for physical entanglements [17].
The rubber samples were swollen in deuterated cyclohexane in 20 mm diameter NMR tubes for 1-2 days prior to experimental analysis. All rubber samples were found to reach equilibrium after 1 day, and the results were reproducible over several days of measurement. All spectra were transferred to a DEC Microvax III+ for analysis. The relaxation time constants were calculated using a non-linear least squares program written in FORTRAN 77. For the aliphatic resonance, a small component was found with an extremely long T2 value of 132 ms. This component was attributed to non-deuterated solvent and low molecular weight additives present in the original formulation, and has been observed in other systems [4]. This component was subtracted out in all calculations.

Calculation of correlation times was aided by the use of the SYBYL molecular modeling programs. A 5 monomer structure was used for these calculations. The conformational energy of this structure was minimized, and the nearest neighbor proton-proton distances were measured for the center monomer unit. From this, an effective radius was calculated. A fuller description of the calculation of the effective radius is provided in Appendix I.
III. RESULTS

Vulcanized cis-polyisoprene samples were analyzed by a Carr-Purcell spin-echo pulse sequence to obtain T2 time constants. Biexponential decay was found for both the olefinic and aliphatic resonances, as is shown in Figure 3 for the aliphatic resonance of a conventional formulation sample cured for 46 minutes (65% cure). Mixed exponential and gaussian behavior was found only for the uncured material. The two components of the biexponential decay are designated T2 short (T2s) and T2 long (T2l). The percentage of T2 short was found to vary directly with the percent of cure, and with the amount of sulfurization up to 0.15% sulfurization. The conventional, semi-efficient and efficient systems all exhibited similar values for T2 short, T2 long and percent of T2 short. Correlation times calculated for the olefinic and aliphatic peaks exhibited excellent agreement. A factor of 10 difference between the correlation times for the slow and fast motions was found.
IV. DISCUSSION

The effect of sulfurization on the T2 relaxation behavior gives direct insight into the mobility changes of an elastomer as a function of cure. The three formulations analyzed were cured to the same extent of cure, yet contained varying amounts of sulfurization [15]. This allowed determination of the effect of sulfurization on the T2 relaxation behavior. Additionally, the ability to resolve the olefinic and the aliphatic resonances supplied two distinct resonances for probing the motional behavior.

Figure 4 shows the observed proton spectrum of the conventional formulation at full cure swollen in deuterated cyclohexane. The aliphatic and olefinic resonances are labeled. It should be noted that the aliphatic resonance is a combination of methylene and methyl resonances. Thus, any correlation time derived from the aliphatic resonance will be a weighted average of the methyl and methylene resonances. This is explained in detail in Appendix I.
Figures 5 and 6 show the change in the T2s (T2 short) value for the olefinic and aliphatic protons as a function of percent cure. The value of T2s for the olefinic proton reaches a minimum at approximately 40 minutes cure time, while the aliphatic proton is constant as a function of cure time. The dependence of the T2s of the olefinic peak on cure time is probably due to a slight perturbation of the chain upon crosslinking, which modifies the proton nearest neighbor distances for the olefinic proton. The aliphatic carbons have a greater ability to rotate, and are thus less sensitive to this effect.

Figure 7 illustrates the change in the percent of T2s as a function of percent cure for the olefinic and aliphatic resonances. Both resonances show a direct correlation between percent cure and percent T2s. Thus, the percent of T2s can be used as a measure of percent cure.

Table II shows a comparison between the three formulations. All three formulations illustrate similar T2s and percent T2s values. All three formulations were shown in past work [15] to have similar chemical microstructures but vary in the amount of sulfurization. There is less cyclization and other non-crosslink structures in the semi-efficient and
efficient systems, yet the same T2s and percent T2s are observed. The logical conclusion to be drawn from this is that crosslink structures play a much greater role than cyclic structures in affecting the T2 relaxation behavior.

Greater insight into the motional behavior of the rubber network is gained by calculation of average correlation times from the T2 values. The specifics of the calculations are discussed in Appendix I. The results, which are shown in Table III, illustrate that the correlation times are roughly $1.6 \times 10^{-7}$ sec for the slow motions and $2.5 \times 10^{-8}$ sec for the fast motions. The agreement between the aliphatic and olefinic protons is quite good. It is interesting to note that the difference in correlation time between the crosslinked and uncrosslinked chains is an order of magnitude.

Variations in the average $r_{HH}$ value was listed as the reason for the dependence of T2s on percent cure for the olefinic peak (Figure 5). The change in $r_{HH}$ that would be required is from 0.212 nm to 0.224 nm, which is a decrease of only 5.8%. This small difference makes this hypothesis very plausible.
It should be noted that there is a slight dependence of the $\%T2_s$ and $T2_s$ values on the extent of sulfurization as can be seen in Table II. Due to the level of the experimental error it is not possible to state definitively that these changes are real, but the fact that they occur for both the aliphatic and olefinic resonances suggests that this is a real phenomenon. The decrease in the $\%T2_s$ and the increase in $T2_s$ with increasing sulfurization is probably due to the modification of the motions by the cyclic groups. Cyclic groups thus appear to slightly impact the range of the motional behavior and also slow down the rate of motion (increase the value of $\tau_c$). This would be expected as cyclic reactions induce increased rigidity in the chain backbone.
V. CONCLUSIONS

The spin-spin relaxation parameters are very sensitive probes of the motional changes during vulcanization. Crosslink structures exhibit a much greater effect on T2 behavior than cyclic and other non-crosslink structures. Two distinct motions are observed in the T2 experiments; a slow and fast motion. The slow motion is related to crosslinked regions while the fast motion is related to mobile regions. The correlation time differences between these regions is a factor of 10. The percent of slow motional regions varied directly with the percent cure for the conventional formulation.
VI. ACKNOWLEDGEMENTS

The authors wish to acknowledge the Rubber Chemicals Division of Monsanto Corporation for supplying the elastomeric samples for this research.
VII. REFERENCES


9. R. Folland, A. Charlesby, Polymer, 20, 207 (1979)

10. R. Folland, A. Charlesby, Polymer, 20, 211 (1979)


**TABLE I**

**CIS-POLYISOPRENE FORMULATIONS**

<table>
<thead>
<tr>
<th>Material</th>
<th>Conventional</th>
<th>Semi-Efficient</th>
<th>Efficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natsyn 2200</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td>Santocure NS</td>
<td>0.75</td>
<td>1.50</td>
<td>3.00</td>
</tr>
<tr>
<td>(TBBS)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfur</td>
<td>2.38</td>
<td>1.50</td>
<td>1.08</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>5.00</td>
<td>5.00</td>
<td>5.00</td>
</tr>
<tr>
<td>Stearic Acid</td>
<td>3.00</td>
<td>3.00</td>
<td>3.00</td>
</tr>
<tr>
<td></td>
<td>%T2s</td>
<td>OLEFINIC T2s(ms)</td>
<td>T21(ms)</td>
</tr>
<tr>
<td>------------------</td>
<td>------</td>
<td>-----------------</td>
<td>---------</td>
</tr>
<tr>
<td>Conventional</td>
<td>90 ± 4</td>
<td>2.5 ± 0.2</td>
<td>17 ± 5</td>
</tr>
<tr>
<td>Semi-Efficient</td>
<td>92 ± 3</td>
<td>2.4 ± 0.1</td>
<td>18 ± 8</td>
</tr>
<tr>
<td>Efficient</td>
<td>94 ± 2</td>
<td>2.3 ± 0.2</td>
<td>15 ± 3</td>
</tr>
</tbody>
</table>
## TABLE III
AVERAGE CORRELATION TIMES

<table>
<thead>
<tr>
<th></th>
<th>T2 (ms)</th>
<th>( r_{HH} ) (nm)</th>
<th>( \tau_c \times 10^8 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Olefinic</td>
<td>2.4 ± 0.2</td>
<td>0.212</td>
<td>16 ± 1</td>
</tr>
<tr>
<td>T2 short</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aliphatic</td>
<td>1.6 ± 0.2</td>
<td>0.200</td>
<td>16 ± 2</td>
</tr>
<tr>
<td>T2 short</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Olefinic</td>
<td>17 ± 5</td>
<td>0.212</td>
<td>2.1 ± 0.8</td>
</tr>
<tr>
<td>T2 long</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aliphatic</td>
<td>9 ± 3</td>
<td>0.200</td>
<td>3 ± 1</td>
</tr>
<tr>
<td>T2 long</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 1: Carr-Purcell spin-echo pulse sequence used for measuring the T2 relaxation behavior.
Figure 2: Rheometer traces for conventional, semi-efficient and efficient formulations
Figure 3: Typical biexponential signal intensity decay for a cured cis-polyisoprene sample.
Figure 4: Proton spectrum of conventional formulation sample at full cure illustrating the proton aliphatic and olefinic resonances.
Figure 5: Change in the T2s value for the olefinic proton as a function of cure time.
Figure 6: Change in the T2s value for the aliphatic proton as a function of cure time.
Figure 7: Change in the percent T2s as a function of percent cure for the olefinic and aliphatic peaks.
Figure 8: Change in the percent T2s as a function of percent sulfurization for the olefinic and aliphatic resonance.
Calculation of the correlation time from the T2 values was performed using the original theories developed by Bloembergen, Purcell and Pound [18]:

$$\frac{1}{T2} = \frac{3\gamma^4 n^2}{20\tau^6} \left[ 3\tau + \frac{5\tau}{1+\omega^2 \tau^2} + \frac{2\tau}{1+4\omega^2 \tau^2} \right]$$  \hspace{1cm} (1)

This equation is valid for dipolar relaxation by intramolecular reorientation, and assumes a single correlation time. While it is well known that polymers contain a distribution of correlation times, the ability of this very simple model to describe our data lead to our decision to use this approximation. The simplicity of this model allows insight into the relationship between network formation and relaxation behavior in these samples.

Calculation of the correlation time $\tau_c$ requires knowledge of the distance over which the relaxation occurs. Calculation of the distance $r_{HH}$ was performed through the use of the molecular modeling packing SYBYL on a Silicon Graphics IRIS system. The package is a commercially available molecular modeling program from Evans and Southerland.
A model of the cis-polyisoprene chain was constructed consisting of 5 monomer units. The minimum energy conformational state was then calculated. From this state the nearest neighbors to the relaxing protons were measured for the center isoprene unit. From the \( r_{HH} \) values of the nearest neighbors the correlation time was calculated as shown below.

For each of the protons there are several nearest neighbors. Since \((1/T2)\) is a rate, the total rate will be the sum of the individual rates:

\[
\frac{1}{T2} = \sum_{i} \frac{3\gamma^4 n^2}{20r^6} \left[ 3\tau + \frac{5\tau}{1+\omega^2 \tau^2} + \frac{2\tau}{1+4\omega^2 \tau^2} \right] \tag{2}
\]

Since several terms in the equation has no dependence on \( r_{HH} \), they can be brought outside the summation. This leaves us with:

\[
\frac{1}{T2} = \frac{3\gamma^4 n^2}{20} \left[ 3\tau + \frac{5\tau}{1+\omega^2 \tau^2} + \frac{2\tau}{1+4\omega^2 \tau^2} \right] \sum_{i} \frac{1}{r^6} \tag{3}
\]

From this we can define a radius \( r_{eff} \), as in

\[
\frac{1}{r_{eff}^6} = \sum_{i} \frac{1}{r^6} \tag{4}
\]
The aliphatic resonance consists of several overlapped resonances. After calculating $r_{\text{eff}}$ for each of the overlapped resonances, we then add the terms together weighting each term according to the number of protons in that resonance. For the aliphatic peak the total rate ($R_{\text{tot}}$) expression is

$$R_{\text{tot}} = \frac{2}{7} R_{\text{eff}}(\text{CH}_2) + \frac{2}{7} R_{\text{eff}}(\text{CH}_2) + \frac{3}{7} R_{\text{eff}}(\text{CH}_3)$$

We can sum over the $r_{\text{eff}}$ for each resonance. This is done as above; thus, we can define a $r_{\text{eff}}$ for the sum of the three protons:

$$\frac{1}{r_{\text{eff}}} = \sum_{\text{F}} \frac{1}{r_{\text{eff}}^{\text{F}}}$$

This provides the final $r_{\text{eff}}$ for use in the calculation of $\tau_c$. 


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