Project #: E-19-689  
Cost share #: 

Center #: 10/24-6-R7394-0A0  
Center shr #: 

Contract#: AGREEMENT DTD 1/13/92  
Prime #: 

Subprojects ? : N 
Main project #: 

Project unit: CHEM ENGR  
Unit code: 02.010.114 

Project director(s): SCHORK F J  

Sponsor/division names: E I DUPONT DE NEMOURS CO  
Sponsor/division codes: 204 / 008 

Award period: 920201 to 930131 (performance) 930131 (reports) 

Sponsor amount  
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Funded 36,488.00  
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Title: G-TYPE NEOPRENE LATEX AGING 

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Security class (U,C,S,TS) : U  
ONR resident rep. is ACO (Y/N): N  
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N/A supplemental sheet  
Equipment title vests with: Sponsor 
NONE PROPOSED.  

Administrative comments -  
INITIATION OF PROJECT. NOTE: THERE IS A PROPRIETARY AGREEMENT ON THIS PROJECT. SPONSOR INVOICED FOR ADVANCE PAYMENT OF $9,000.
NOTICE OF PROJECT CLOSEOUT

Closeout Notice Date 08/05/93
Project No. E-19-689
Project Director SCHORK F J
School/Lab CHEM ENGR
Sponsor E I DUPONT DE NEMOURS CO/
Contract/Grant No. AGREEMENT DTD 1/13/92
Prime Contract No.
Title G-TYPE NEOPRENE LATEX AGING
Effective Completion Date 930131 (Performance) 930131 (Reports)

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Comments: EFFECTIVE DATE 2-1-92. CONTRACT VALUE $36,488.

Subproject Under Main Project No.
Continues Project No.

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MODELING THE ALKALINE AGING
OF G-TYPE NEOPRENE LATEXES

A Report Prepared for
E.I. du Pont de Nemours and Company
Polymer Products Department

June 22, 1993

Work Done by: C.L. Liotta, F.J. Schork, C.M. Gilmore (author)
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ABSTRACT

G-Type Neoprene alkaline aging has been mathematically modeled based on a simplified mechanism involving simultaneous branching, scission and capping reactions. With key assumptions involving the unpeptized polymer MWD, molecular weight predictions, calculated from the leading moments of the polymer chain distributions, agree with experimental profiles and exhibit the expected sensitivity to peptizing agent concentrations. Residual peptizing agent and reactive site predictions are also consistent with analytical findings, but the observed particle size sensitivity is not fully explained by mass transfer effects.
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INTRODUCTION

The objective of this work, commissioned by DuPont to Georgia Tech [1], was to identify and mathematically model the mechanisms governing G-Type Neoprene alkaline aging, with the ultimate goal of facilitating quality improvement.

This report details progress made toward the accomplishment of this objective. The proposed mechanism[2] is restated, followed by the detailed mathematical model development, from the mass balances to the molecular weight moment equations. Finally, model validity is checked by comparison with laboratory data, and model sensitivity and predictive capability are assessed.

SUMMARY AND CONCLUSIONS

This report documents the progress of Georgia Tech personnel commissioned to 1) aid in the mechanistic understanding of G-Type Neoprene alkaline aging, and 2) produce a mathematical model of the associated peptization reactions.

In practice, G-Type Neoprene latex aging curves generally first exhibit a decrease, followed by a possible increase in Mooney viscosity, and are sensitive to latex particle size. Recent GPC data also suggest a sensitivity to the unpeptized polymer molecular weight distribution (MWD), as some peptization curves are characterized by an initial increase in molecular weight. While the details of this early increase are unresolved, mechanistically, the Mooney viscosity and molecular weight trends may be explained by a few key simultaneous scission, branching and capping reactions. Specifically, chain scission at the polysulfide sites is accomplished by the attack of dithiocarbamates (derived from tetraethylthiuram disulfide, TETD, or N,N-dibutyldithiocarbamate, Tepidone) on the sulfur-sulfur linkages of the copolymer. Branching results from the nucleophilic attack of a polymeric sulfide ion (derived from the scission reaction) on an allylic chloride or vinyl chloride group of another chain. Alternatively, the polymeric sulfide ion may be capped by reaction with TETD. The TETD/Tepidone ratio controls the capping/scission rate and thus determines molecular weight evolution. The mechanism is complicated by possible reversibility of the scission and capping reactions, and particle/aqueous-phase interfacial reactions.

The subject model (Model I) neglects these complications and also assumes that the unpeptized polymer is uniformly aged in a single well-mixed batch, is uniform with respect to reactive sites, and is characterized by a
unimodal MWD. The latex is assumed monodisperse, and the particle phase homogeneous. Tepidone uptake is modeled as a mass transfer resistance at the particle/aqueous-phase interface. Efforts aimed at relaxing some of these assumptions are reported separately (Models II, III).

Based on these assumptions, mass balances for the two polymer populations (uncharged and polymeric sulfide ions), reactive site, and peptizing agent concentrations were used to generate equations describing the three leading moments of each MWD. Model I then, comprised of 12 coupled ODEs, predicts the polymer weight and number-average molecular weights, and the Tepidone, TETD, and reactive site concentrations versus aging time. Major user-specified parameters, in addition to the recipe and other physical constants, include the latex and unpeptized polymer properties (e.g. $MW_w$, $MW_n$, $D_p$), rate constant Arrhenius parameters and medium correction factors, and Tepidone mass transfer parameters.

Model I predicted the laboratory peptization behavior of G-Type polymers that did not exhibit a large MW increase early in peptization (indicative of a persistent multimodal MWD with a preponderance of low MW chains). The $MW_w$ and residual TETD profiles were in good agreement with measured values, and the predicted residual allylic chloride and $S_6$ site levels were qualitatively consistent with analytical findings.

Model I predictions of TETD and Tepidone effects were consistent with empirical observations and the proposed mechanism, i.e. the TETD/Tepidone ratio controlled the capping/scission rate and thus determined molecular weight evolution. Increasing the Tepidone level at a fixed, sufficient TETD concentration decreased $MW_w$, as did increasing the TETD level at a fixed Tepidone concentration.

Model I predictions of peptization rate were most sensitive to the scission rate constant and Tepidone level, while minimum $MW_w$ predictions were sensitive to the capping and branching (allylic chloride only) rate constants. Increased/decreased sulfur incorporation was also observed to decrease/increase the final $MW_w$, while peptization rate predictions were also sensitive to the Tepidone partition coefficient, with an increase in affinity for the particle phase causing an increase in peptization rate. Order of magnitude changes in the Tepidone mass transfer coefficient also impacted peptization rate. However, with the monodispersed latex assumption, ±20% changes in the average particle diameter did not significantly affect Tepidone transfer.
RECOMMENDATIONS

- Model I use for general understanding of peptization variables.
- Model I use to aid development of peptization analytical techniques.
- Couple Model I with existing software to predict RTD effects.
- Continued model development to merge peptization chemistry and multimodal unpeptized polymer MWD.
- Analyze particle size effects with polydisperse latex.
DISCUSSION OF RESULTS

Mathematical modeling of a given process typically entails first, identification of the governing mechanisms, second, statement of the associated reaction kinetics, third, expression of the necessary mass and/or energy balances, fourth, application and/or development of appropriate mathematical solution techniques, and lastly, verification of the model predictions. This modeling strategy (Figure 1) was applied to the G-Type Neoprene alkaline aging process. Results are presently discussed.

![Modeling Schematic](image)

Figure 1: Modeling Schematic

I. Process Description

A. Reactor Configuration

In practice, G-Type Neoprenes may be aged over several vessels, and polymer exiting a given vessel is characterized by a residence time distribution. The subject model neglects these complications, and assumes the polymer is uniformly aged in a single well-mixed batch. Multiple vessel and non-ideal flow complications may be handled separately by solving the subject model in conjunction with suitable software.
B. Reaction Mechanism and Kinetics

Experimentally, G-Type Neoprene latex aging curves generally first exhibit a decrease, then an eventual increase in Mooney viscosity (Figure 2), and are sensitive to latex particle size. Note, however, that some experimental data[3] show an early increase in MW, followed by the expected MW decrease. This data supports characterization of the peptization process by simultaneous MW-decreasing and MW-increasing reactions. As depicted in Figure 2, chain scission at the polysulfide sites is thought to dominate when the Mooney decreases, and branching and/or other MW-increasing reactions dominate when the viscosity increases. A proposed aging mechanism, accounting for simultaneous peptization/capping/branching and interphase mass transfer, has been reported[2], but is restated here (with some additions) for continuity.

Figure 2: G-Type Neoprene Aging Curve (illustrative)

The reactions, listed in Table 1, represent three basic mechanisms: nucleophilic attack, acid-base equilibrium, and oxidation. Nucleophilic attack is the dominant mechanism and may involve the attack of several nucleophiles (dithiocarbamate \((T^-)\), hydroxide ion \((OH^-)\), polymeric sulfide ion \((S^- M_q)\)) on electrophilic disulfide bonds (chloroprene-sulfur copolymer \((M_n)\), tetraethylthiuram disulfide \((TETD, TT)\), mixed disulfide \((T_0 T_e)\)). Note that \(M_n\) is of arbitrary length and may be part of a branched network. Also, as depicted by the schematic in Figure 3, the reactions may occur in the particle phase and/or at the particle-aqueous phase interface, depending on the solubility of the involved species.

---

1As presented in Section IV.C., the author assumes a general positive correlation of Mooney viscosity with MW (Figure 23), realizing that Mooney viscosity actually depends on parts of the MWD and the peptization reactions occurring in the Mooney apparatus.

2Other unidentified reactions probably occur during peptization. Ongoing NMR studies suggest, at least, the formation of diethylamine[4].
Table 1: G-Type Neoprene Alkaline Aging — Proposed Mechanism[2]

<table>
<thead>
<tr>
<th>#</th>
<th>Reaction</th>
<th>Type</th>
<th>Site</th>
<th>Other Comments</th>
</tr>
</thead>
</table>
| 1  | $M_n + T^- \xrightarrow{k_1} S^-M_q + M_{n-q}T$                         | NA   | P,I  | • Primary scission reaction  
|    |                                                                          |      |      | • Occurs at any sulfur (except RS bond)                                         |
| 1a | $M_n + OH^- \xrightarrow{k_{1a}} S^-M_q + M_{n-q}OH$                     | NA   | I    | • OH$^-$ insoluble in particle phase                                            |
| 2  | $M_n + S^-M_q \xrightarrow{k_2} M_r + S^-M_m$                           | NA   | P    | • Molecular weight redistribution                                              |
| 3  | $M_n + S^-M_q \xrightarrow{k_3} M_{n+q} + Cl^-$                          | NA   | P    | • Allylic chloride (cis 1,2 isomer)                                            |
|    |                                                                          |      |      | • Branching reaction                                                          |
|    |                                                                          |      |      | • Tepidone sink                                                               |
| 3a | $M_n + T^- \xrightarrow{k_{3a}} M_n + Cl^-$                             | NA   | I    | • TT may be mixed disulfide                                                   |
| 4  | $TT + OH^- \xrightarrow{k_4} T^- + TOH$                                 | NA   | I    | • Disulfide exchange                                                          |
|    |                                                                          |      |      | • Occurs between any dithiocarbamate and any thiuram disulfide                 |
|    |                                                                          |      |      | • Various sulfide ions kinetically indistinguishable                           |
| 5  | $T_eT_e + T_b \xrightarrow{k_5} T_bT_e + T_e^-$                          | NA   | P,I  | • Vinyl chloride                                                              |
|    |                                                                          |      |      | • Branching reaction                                                          |
|    |                                                                          |      |      | • k$_7$ small, but [VC] large                                                  |
| 6  | $TT + S^-M_q \xrightarrow{k_6} T^- + TSM_q$                             | NA   | P    | • Occurs with any thiuram disulfide                                            |
| 7  | $M_n + S^-M_q \xrightarrow{k_7} M_{n+q} + Cl^-$                          | NA   | P    | • Hydrolysis of polymeric sulfide ion                                          |
|    |                                                                          |      |      | • Vinyl chloride                                                              |
|    |                                                                          |      |      | • Branching reaction                                                          |
|    |                                                                          |      |      | • k$_7$ small, but [VC] large                                                  |
| 8  | $RS^- + H_2O \xrightarrow{k_8} RSH + OH^-$                              | ABE  | I    | • Oxidation of polymeric sulfide ions                                          |
| 9  | $2RS^- + 2O_2 + 2H_2O \xrightarrow{k_9} RSSR + H_2O_2 + 2OH^-$           | OXD  | I    | • Oxidation of polymeric sulfide ions                                          |

*Mechanism type: NA – nucleophilic attack, ABE – acid-base equil., OXD – oxidation

*Physical site of reaction: P – particle phase, I – particle interface
The deceptively simple Table 1 reaction set actually encompasses complex equilibrium reactions and polymer structure/reactivity complications. Consider Reactions 1 and 2.

\[ M_n + T^- \rightleftharpoons k_1 M_{n-q}T + S^-M_q \]
\[ M_n + S^-M_q \rightleftharpoons k_2 M_r + S^-M_m \]

The capped chain from Reaction 1 \((M_{n-q}T)\) may react with a polymeric sulfide ion \((S^-M_q)\) according to Reaction 2. If the polymeric sulfide ion attacks the terminal sulfur linkage of the capped chain, a higher MW chain and a pseudo Tepidone are formed, i.e.

\[ M_{n-q}T + S^-M_q \rightleftharpoons k_3 M_n + T^- \]

This is, in effect, the reverse of Reaction 1. Similarly, consider Reactions 6 and 1.

\[ TT + S^-M_q \rightleftharpoons k_4 M_qT + T^- \]
\[ M_n + T^- \rightleftharpoons k_5 M_{n-q}T + S^-M_q \]

The capped chain from Reaction 6 \((M_qT)\) may react with Tepidone \((T^-)\) according to Reaction 1. If Tepidone attacks the terminal sulfur linkage of the capped chain, a polymeric sulfide ion and a pseudo thiuram are formed, i.e.

\[ M_qT + T^- \rightleftharpoons k_6 S^-M_q + TT \]
This is, in effect, the reverse of Reaction 6. Both Reaction 1 and Reaction 6 reverse reactions require chain scission at the terminal polysulfide site. The assumption that the ratio of terminal sites to intramolecular sites is small affords a potential modeling simplification.

The Table 1 reaction set is further complicated by the polymer structure and reactivity. Although conveniently characterized by an average molecular weight, the unpeptized polymer is obviously comprised of a distribution(s) of chain lengths, each potentially varying in intramolecular structure, e.g. allylic Cl sites, sulfur concentration and sequence length distribution. Thus, the polymer MWD may be uni- or multi-modal, and the reaction rate constants are functions of the number of sulfurs in the polysulfide linkage (sulfur rank).

Finally, in addition to the Table 1 reaction set, the proposed peptization mechanism accommodates dithiocarbamate (Tepidone, $T^-$) transfer from the aqueous phase into the particle:

$$ (T^-)_{aq} \stackrel{k_{ma}}{\longrightarrow} (T^-)_{particle} $$

The electrostatic double layer at the particle surface presents a resistance to transfer of the sulfide ion across the interface. According to this model, Tepidone uptake is governed by 1) the equilibrium partitioning of Tepidone between the particle and aqueous phases, 2) mass transfer resistance at the particle surface ($k_{ma}$), and 3) the rate of reaction of Tepidone inside the particle. Other, possibly less favorable, mechanisms are discussed in Reference [2].
II. Mathematical Model Development

A. Mechanistic Assumptions

As is evident from the proposed mechanism, the simplest of polymeric processes are often very complex, necessitating simplifying assumptions for successful modeling. The subject aging models incorporate several key assumptions (Table 2). The base assumptions apply to all models, while further simplifications are model-specific. Key assumptions requiring further elaboration are presently discussed. Minor assumptions (not listed in Table 2) are stated as appropriate in the subsequent text.

<table>
<thead>
<tr>
<th>Model Assumptions</th>
<th>Model I</th>
<th>Model II</th>
<th>Model III</th>
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<tr>
<td><strong>Base Assumptions</strong></td>
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<tr>
<td>Monodisperse latex</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
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<tr>
<td>Homogeneous particle phase</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Unpeptized polymer 100% soluble</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
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<td>Indistinguishable ion rxns negl.</td>
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<td>✓</td>
<td>✓</td>
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<tr>
<td>Uniform allylic Cl</td>
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<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Chain scission arbitrary</td>
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<td>✓</td>
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<td>Average rate constants</td>
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<tr>
<td><strong>Other Simplifications</strong></td>
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<tr>
<td>Interfacial rxns negl.</td>
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<tr>
<td>Unimodal MWD</td>
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<tr>
<td>Uniform sulfur dist.</td>
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<tr>
<td>Scission at end site negl.</td>
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<tr>
<td>Reactions 1',2' negl.</td>
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<td></td>
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<tr>
<td>Capped/Uncapped negl.</td>
<td></td>
<td></td>
<td>✓</td>
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<tr>
<td>(i.e. (M_nT=M_n))</td>
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<td></td>
<td>✓</td>
</tr>
<tr>
<td>Tepidone sink (allylic Cl) negl.</td>
<td>✓</td>
<td></td>
<td></td>
</tr>
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</table>
Base Assumptions (all models)

The unpeptized polymer is present in latex particles which are assumed spherical and of uniform diameter and composition. Relaxing the monodisperse PSD assumption does not significantly complicate modeling equations, but computation time is increased since the equations are solved repeatedly for several particle sizes. On the other hand, the homogeneous particle phase assumption avoids the complexity of partial differential equations since any radial dependence of species concentrations is neglected. This assumption is potentially significant since several reactions involve partially water-soluble species.

The unpeptized polymer is further assumed to be 100% soluble[3]. This is in contrast to earlier thought that a fraction of the polymer was insoluble, presumably due to crosslinking and/or excessive entanglement. A given polymer chain is assumed uniform with respect to intramolecular branching sites (e.g. allylic Cl) and polysulfide linkages. Allylic Cl may be relatively evenly distributed, but sulfur is probably not uniformly incorporated during polymerization[5]. Nonetheless, with the assumption of uniform intramolecular sulfur distribution, scission may occur arbitrarily at any site along the chain. The polysulfide linkages may contain 2 to 8 sulfurs, but the \( S_6 \) configuration appears prevalent[6], and is therefore assumed exclusively. Accordingly, average rate constants are used, but compensation is made for a general reduction in rate constants with decreased sulfur rank.

Other Assumptions (model-specific)

While all of the subject models incorporate the base assumptions, they may be distinguished based on characterization of the unpeptized polymer MWD and treatment of certain end-chain and interfacial reactions. Specifically, both Models I and II assume that the unpeptized polymer MWD is unimodal, but GPC results[3] show a definite multimodality (Figures 4 and 5), which may (Figure 5) or may not (Figure 4) persist after the onset of peptization. More importantly, peptization appears very sensitive to the unpeptized polymer structure. Thus, Model III assumes a trimodal MWD, and also accommodates an overall variance of sulfur incorporation with polymer molecular weight, i.e. polymer in a given MW fraction may contain more or less sulfur than that in another fraction. This affords a possible means of adjusting relative reactivities without altering rate constants.

Like Model I, however, Model III neglects interfacial reactions (1a,4,8, and 9 in Table 1) and reactions describing scission at the terminal sulfur linkage of a capped chain. First, consider the interfacial reaction assumption. Doyle[7] measured a definite, but slow reduction in Mooney viscosity after adding TETD only to a G-Type Neoprene. This may be explained by the reaction of
Figure 4: MWD(GPC) vs Aging Time for Run 4[3].

Figure 5: MWD(GPC) vs Aging Time for Run 2[3].
TETD with $OH^-$ to yield $T^-$ (Reaction 4), and subsequent chain scission via Reaction 1. The observed slow Mooney reduction (compared to that observed with both TETD and Tepidone added) suggests that Reaction 4, and thus Reaction 1a, may be neglected. Recent GPC measurements\[3\], however, show a significant change in MW after TETD, but before Tepidone addition (Table 3), suggesting the significance of interfacial and/or unidentified reactions. Model II includes Reactions 1a and 4, but assumes a constant low $[OH^-]$. Alternatively, Reaction 4 effects may be estimated by assuming a fraction of the added TETD is lost to $T^-$, perhaps during the quick transfer to the particle phase.

Table 3: Average MW for Unpeptized and Thiuram Only Samples\[3\].

<table>
<thead>
<tr>
<th></th>
<th>Unpeptized</th>
<th>With TETD Only</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run 2 $MW_n$</td>
<td>108,000</td>
<td>105,000</td>
</tr>
<tr>
<td>$MW_w$</td>
<td>854,000</td>
<td>1,408,000</td>
</tr>
<tr>
<td>Run 6 $MW_n$</td>
<td>105,000</td>
<td>114,000</td>
</tr>
<tr>
<td>$MW_w$</td>
<td>1,579,000</td>
<td>625,000</td>
</tr>
</tbody>
</table>

Next consider the reactions describing scission at the terminal sulfur linkage of a capped chain. Specifically,

$$M_nT + T^- \xrightarrow{k'_1} S^-M_n + TT$$

$$M_{n-q}T + S^-M_q \xrightarrow{k_2} M_n + T^-$$

NMR analysis of model compound reactions with Tepidone only\[4,6\] and separate analysis of Tepidone uptake data\[6\] with no TETD added revealed no TETD formation. This suggests that $k_6$ is much larger than $k'_1$, a conclusion also supported by kinetic studies\[6\]. On the other hand, kinetic studies estimated $k'_2$ at roughly an order of magnitude greater than $k_1$ and NMR analysis indicated little capped product in the absence of TETD, both potentially supporting the relative significance of Reaction 2'. NMR results also indicate, however, that the capped product is unstable, somehow decomposing to a polymeric sulfide ion and diethylamine. This suggests that the unidentified decomposition rate constant is larger than $k'_2$, thus explaining the absence of capped product when only Tepidone is added. More pertinent to MW considerations, Reaction 2' may not afford a net MW increase since it would follow Reaction 1 and it is unlikely that a higher MW capped chain or polymeric sulfide ion would preempt the Reaction 1 products. Reaction with a capped product from Reaction 6 would result in a higher MW species, but further chain scission is probable (Reaction 2' also generates a Tepidone) since TETD sustains reduced MW. The net effect of Reaction 2 could be a
higher equilibrium particle-phase Tepidone concentration. Lastly, note that
reaction 2 may effect a MW increase via scission near the chain end, e.g.

\[
M_5 + S_{15}^{-} \xrightarrow{k_2} M_2 + S_{18}^{-}
\]

\[
\begin{array}{c|c|c}
M_n & 10 & 10 \\
M_w & 12.5 & 16.4 \\
\end{array}
\]

Neglecting the end-chain reactions eliminates the need for tracking the capped
species and reduces the number of model equations. Models I and III incor-
porate this simplification, while Model II includes the end-chain reactions.

Finally, consider Tepidone reaction at the allylic Cl (Reaction 3a). While
kinetic measurements[6] support inclusion of this reaction as a true Tepidone
sink, Tepidone uptake measurements (Figure 6) do not show a significant
continual decrease in the aqueous phase Tepidone concentration when allylic
Cl is undoubtedly present[3]. Reaction 3a is omitted from Models I and III,
but is included in Model II.

Figure 6: Tepidone Uptake with Neoprene GRT Latex at 40°C[6].

Many of the model-specific assumptions resulted from mechanistic insight
gained and/or emphasized after modeling efforts were well underway. Thus,
the first model, Model I, has been analyzed most completely, and
is emphasized in subsequent discussion.
B. Fundamental Theories and Derivations

Having proposed the mechanism governing the aging process, and identified key simplifying assumptions, construction of the model equations follows. Here, the fundamental principles of mass balances, discrete transformation, and moment representations are employed. A brief discussion of these principles follows. The reader is referred to References [8]-[10] for more detail.

For this batch system, mass balances are of the form

\[
\begin{align*}
\text{change in concentration} & = \text{total rate of addition or depletion of concentration} \\
& \text{by various mechanisms}
\end{align*}
\]  

(1)

and may be written for the polymer chain populations \((M_n \text{ and } S^- M_n)\), along with other species, to obtain a complete differential molecular weight distribution (MWD).

The mass balances constitute an infinite set \((n \text{ from 1 to } \infty)\) of coupled ordinary differential equations (ODEs). Aside from the obvious calculational difficulties, the routine use of full differential MWDs to represent the state of reacting polymer is often impractical or impossible. It is more convenient to use the leading moments of the differential MWD. For the populations \(M_n\) and \(S_n\), the \(k\)th moments are defined as

\[
\eta_k = \sum_{n=1}^{\infty} n^k M_n \quad k = 0, 1, 2, ...
\]

\[
\lambda_k = \sum_{n=1}^{\infty} n^k S_n \quad k = 0, 1, 2, ...
\]

(2)

and the number and weight-average molecular weights \((MW_n, MW_w)\) as

\[
MW_n = w \left[ x_M \left( \frac{\eta_1}{\eta_0} \right) + x_S \left( \frac{\lambda_1}{\lambda_0} \right) \right]
\]

(3)

\[
MW_w = w \left[ x_M \left( \frac{\eta_2}{\eta_1} \right) + x_S \left( \frac{\lambda_2}{\lambda_1} \right) \right]
\]

(4)

\[
PD = \frac{MW_w}{MW_n}
\]

(5)

where \(w\) is the mer molecular weight and \(x_M\) and \(x_S\) are the weight fractions of the \(M_n\) and \(S_n\) populations, respectively. PD is the polydispersity.

Obviously, the moment equations may be obtained directly from Eqn. (2) by the indicated series summation of the mass balances, i.e.

\[
\frac{d\eta_k}{dt} = \sum_{n=1}^{\infty} n^k \frac{dM_n}{dt}
\]

(6)
but it is generally easier to use a discrete transformation technique, such as Z-transforms, and then extract the moments. Given the population $M_n$, the Z-transform is defined as

$$M(z) = \sum_{n=0}^{\infty} M_n z^{-n} \quad (7)$$

and the infinite set of ODEs is transformed to a single equation for $\frac{dM(z)}{dt}$. The moment equations become

$$\eta_k = \left[ (-1)^k \frac{\partial^k M(z)}{\partial (ln z)^k} \right]_{z=1} \quad (8)$$

or

$$\frac{d\eta_k}{dt} = \frac{d}{dt} \left[ (-1)^k \frac{\partial^k M(z)}{\partial (ln z)^k} \right]_{z=1} \quad (9)$$

and a set of three moment equations ($\frac{d\eta_0}{dt}, \frac{d\eta_1}{dt}, \frac{d\eta_2}{dt}$) replaces the $\frac{dM(z)}{dt}$ equation.

As is the case in many polymer systems, here, the equation for $\eta_2$ depends on $\eta_3$. As pointed out by Tirrell[10], this generally occurs when a polymer participates in a reaction which can occur at every monomer unit along the chain, and not only at the ends. This is the case in Reactions 1 and 2, where the nucleophile ($T^-$ or $S^- M_n$) may attack the polymer chain ($M_n$) at any monomer unit. Tirrell further applies a moment closure procedure using the associated Laguerre polynomials to obtain the following expression for an arbitrary distribution described as a perturbation around a T-distribution:

$$\eta_3 = \frac{\eta_2}{\eta_0 \eta_1} (2\eta_0 \eta_2 - \eta_1^2) \quad (10)$$

With this substitution, the set of moment equations may be solved numerically.

C. Mass Balances

Using the form of Eqn. (1), Model I mass balances are written for the polymer populations ($M_n$ and $S^- M_n$), the polysulfide ($RS$), allylic chloride ($AC$), and vinyl chloride ($VC$) reactive sites, and the Tepidone (aqueous $T_w$, particle $T_p$) and TETD ($TT$) concentrations. Balances are based on the simplified mechanism listed in Table 4.

\(^3\)Substitution of the moment expressions for $M_n$, $M_w$, and $M_s$ into Eqn. (10) yields $M_s = 2M_w - M_n$, an obvious underestimation.
Table 4: G-Type Neoprene Alkaline Aging — Model I Mechanism[2]

<table>
<thead>
<tr>
<th>#</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$M_n + T^- \xrightarrow{k_1} S^-M_q + M_{n-q}T$</td>
</tr>
<tr>
<td>2</td>
<td>$M_n + S^-M_q \xrightarrow{k_2} M_r + S^-M_m$</td>
</tr>
<tr>
<td>3</td>
<td>$M_n + S^-M_q \xrightarrow{k_3} M_{n+q} + Cl^-$</td>
</tr>
<tr>
<td>6</td>
<td>$TT + S^-M_q \xrightarrow{k_6} T^- + TSM_q$</td>
</tr>
<tr>
<td>7</td>
<td>$M_n + S^-M_q \xrightarrow{k_7} M_{n+q} + Cl^-$</td>
</tr>
</tbody>
</table>

Uncharged Polymer Population, $M_n$

Noting that $M_n$, $M_nT$, and $TSM_n$ are equivalent, and $S^-M_n$ may be written as $S_n$ for simplicity, the mass balance on species $M_n$ ($n = 1, 2, \ldots$; $M_0 = S_0 = 0$) is given by

$$\frac{dM_n}{dt} = k_1 T_p f_s \sum_{q=n+1}^{\infty} M_q - k_1 T_p f_s (n - 1) M_n$$

$$+ k_2 f_s \sum_{q=0}^{n-1} S_q \sum_{p=(n-q)+1}^{\infty} M_p - k_2 f_s (n - 1) M_n \sum_{q=1}^{\infty} S_q$$

$$+ k_3 f_a \sum_{q=1}^{n-1} q M_q S_{n-q} - k_3 f_a n M_n \sum_{q=1}^{\infty} S_q$$

$$+ k_7 f_v \sum_{q=1}^{n-1} q M_q S_{n-q} - k_7 f_v n M_n \sum_{q=1}^{\infty} S_q + k_6 [TT] S_n$$

(11)

where $f_s$, $f_a$, and $f_v$ are the fraction of polysulfide linkages, allylic chlorides, and vinyl chlorides in the polymer chain (moles reactive sites/mole mer). The equation form reflects the rate dependence on the number of reactive sites, not the polymer concentration.

Polymeric Sulfide Ions, $S^-M_n$ or $S_n$

The mass balance on species $S_n$ is given by

$$\frac{dS_n}{dt} = k_1 T_p f_s \sum_{q=n+1}^{\infty} M_q + k_2 f_s \sum_{q=1}^{\infty} S_q \sum_{p=n}^{\infty} M_p$$

$$+ k_2 f_s S_n \sum_{p=1}^{\infty} p M_p - k_3 f_a S_n \sum_{q=1}^{\infty} q M_q$$

$$- k_7 f_v S_n \sum_{q=1}^{\infty} q M_q - k_6 [TT] S_n$$

(12)
Polysulfide Reactive Sites, $[RS]$

The mass balance on the polysulfide reactive sites is potentially complicated by the fact that each linkage of 3 or more sulfurs provides more than one reactive site. Thus, the effect of each of the reactions on $[RS]$ depends upon the length of the sulfur linkages in $M_n$ and $S_q$, and/or where the scission occurs. For example, as indicated below, for a given scission, Reaction 2 could increase, decrease, or not affect $[RS]$.

$$R_1 - S_4^- + R_2 - S_6^- - R_3$$ (5 sites)

$$\xrightarrow{k_2} R_1 - S_5^- - R_2 + R_3 - S_5^-$$ (7 sites)

$$\xrightarrow{k_3} R_1 - S_5^- - R_2 + R_3 - S_6^-$$ (4 sites)

$$\xrightarrow{k_4} R_1 - S_5^- - R_2 + R_3 - S_4^-$$ (5 sites)

In the above example, the composition of $R_1$, $R_2$ and $R_3$ also affect $[RS]$.

To avoid this complexity, the balance is written for the polysulfide linkage concentration, effectively assuming each linkage provides one reactive site. Thus,

$$\frac{d[RS]}{dt} = -k_1 T_0 f_s \sum_{n=1}^{\infty} (n - 1) M_n + k_3 f_a S_n \sum_{q=1}^{\infty} q M_q$$

$$+ k_6 [TT] \lambda_0 + k_7 f_s S_n \sum_{q=1}^{\infty} q M_q$$

(13)

To convert $[RS]$ (mole sites/cc-part) to $f_s$ (mole sites/moles mer), divide by the total mer concentration, i.e.

$$f_s = \frac{[RS]}{\eta_1 + \lambda_1}$$

(14)

Eqn. (15) affords a virtual conservation of reactive sites and necessitates an independent reduction of rate constants with sulfur rank reduction. Alternatively, one might track the depletion of $S_6$ linkages via Reaction 1 only, and assume each $S_6$ scission yields two less reactive $S_2$, $S_3$, or $S_4$ linkages. A reduced rate constant ($k_{1,red} = k_1 \cdot \text{reduction factor}$) would then apply to the low sulfur rank sites, and $k_1 f_s$ would be expanded to $[k_1 f_s + 2k_{1,red}(f_{so} - f_s)]$ in the other rate expressions. The Model I code reflects this alternate approach; for brevity, $k_1 f_s$ is not expanded in the text. A similar treatment is applied to $k_2 f_s$.

Allyl Chloride Sites, $[AC]$

Allyl chloride sites in the soluble fraction are expressed by

$$\frac{d[AC]}{dt} = -k_3 f_a S_n \sum_{q=1}^{\infty} q M_q$$

(15)
where
\[ f_a = \frac{[AC]}{\eta_1 + \lambda_1} \] (16)

**Vinyl Chloride Sites, [VC]**

Vinyl chloride sites in the soluble fraction are expressed by
\[ \frac{d[VC]}{dt} = -k_f f_v S_n \sum_{q=1}^{\infty} qM_q \] (17)

where
\[ f_v = \frac{[VC]}{\eta_1 + \lambda_1} \] (18)

**Tepidone, \( T_w \) and \( T_p \)**

By assumption, the Tepidone is initially present in the aqueous phase \( (T_w) \), and then transfers to the particle \( (T_p) \), the driving force being the departure from equilibrium concentrations. \( T_w \) is given by
\[ \frac{dT_w}{dt} = -\frac{k_m A_p}{V_w} \left[ T_w - \left( \frac{1}{PC} \right) T_p \right] \] (19)

where \( PC \) is the partition coefficient, i.e. \( (T_p/T_w)_{equil} \). Similarly, Tepidone enters the particles at the same rate, is consumed by Reaction 1, and produced by Reaction 6. Thus,
\[ \frac{dT_p}{dt} = \frac{k_m A_p}{v_p} \left[ T_w - \left( \frac{1}{PC} \right) T_p \right] - k_1 T_p f_s \sum_{n=1}^{\infty} (n - 1)M_n + k_6 [TT] \sum_{n=1}^{\infty} S_n \] (20)

**Tetraethylthiuram Disulfide, [TT]**

By assumption, TETD is exclusively in the particle phase at the beginning of peptization. It is consumed by Reaction 6. Thus,
\[ \frac{d[TT]}{dt} = -k_6 [TT] \sum_{n=1}^{\infty} S_n \] (21)
### Table 5: Z-Transforms

<table>
<thead>
<tr>
<th>Function</th>
<th>Z-Transform</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_n$</td>
<td>$M(z) = \sum_{n=0}^{\infty} M_n z^{-n}$</td>
</tr>
<tr>
<td>$c$</td>
<td>$c\left(\frac{z}{z-1}\right)$</td>
</tr>
<tr>
<td>$\sum_{q=1}^{n} M_q$</td>
<td>$M(z)\left(\frac{z}{z-1}\right)$</td>
</tr>
<tr>
<td>$nM_n$</td>
<td>$-z^{\frac{\partial M(z)}{\partial z}}$</td>
</tr>
<tr>
<td>$\sum_{q=1}^{n-1} qM_q S_{(n-q)}$</td>
<td>$-S(z)^{\frac{\partial M(z)}{\partial z}}$</td>
</tr>
</tbody>
</table>

### D. Discrete Transformation, Moment Equations

As outlined in Section II.B., the infinite set of mass balances is transformed to a finite, solvable set by employing Z-transforms, and the associated moment generation property. Using the Z-transforms in Table 5 and the moment definitions in Eqn. (2), each term in Eqns. (13) and (14) is transformed to yield

$$\frac{dT(t)}{dt} = k_1 f p \left( \frac{\eta_0 + z \Lambda(z)}{z-1} \right) - k_1 f p \left[ \sum_{n=1}^{\infty} n z^{-n} M_n - \Lambda(z) \right]$$

$$+ E \left[ k_2 f p \sum_{q=0}^{n-1} S_q \sum_{p=(n-q)+1}^{\infty} M_p \right] - k_2 f p \lambda_0 \left[ \sum_{n=1}^{\infty} n z^{-n} M_n - \Lambda(z) \right]$$

$$+ k_3 f a S(z) \left( \sum_{n=1}^{\infty} n z^{-(n+1)} M_n \right) - k_3 f a \lambda_0 \sum_{n=1}^{\infty} n z^{-n} M_n$$

$$+ k_7 f u S(z) \left( \sum_{n=1}^{\infty} n z^{-(n+1)} M_n \right) - k_7 f u \lambda_0 \sum_{n=1}^{\infty} n z^{-n} M_n$$

$$+ k_0 [TT] S(z)$$

Equation (22) is transformed to yield
and
\[
\frac{dS(z)}{dt} = k_1 T_p f_s \left( \frac{\eta_0 - z M(z)}{z - 1} \right) + k_2 f_s \lambda_0 \left( \frac{\eta_0 - z M(z)}{z - 1} \right) - k_6 [TT] S(z)
\]
\[-k_2 f_s (\eta_1 - \eta_0) S(z) - k_3 f_s \eta_1 S(z) - k_7 f_\nu \eta_1 S(z)
\]
\[= k_1 T_p f_s \left( \frac{\eta_0 - z M(z)}{z - 1} \right) + k_2 f_s \lambda_0 \left( \frac{\eta_0 - z M(z)}{z - 1} \right) - k_6 [TT] S(z)
\]
\[ -k_2 f_s (\eta_1 - \eta_0) S(z) - k_3 f_s \eta_1 S(z) - k_7 f_\nu \eta_1 S(z)
\]
(23)

The Z-transform of the third term in Eqn. (11) is not easily identified, so the contribution to the moment equations is calculated directly from the mass balance (Eqn. (6)). For the remaining terms, the moment contributions are calculated by evaluating Eqn. (9). Specifically, for Eqn. (22),
\[
\frac{d\eta_0}{dt} = \frac{dM(z)}{dt} |_{z=1}
\]
\[
\frac{d\eta_1}{dt} = \frac{d}{dt} \left( -z \frac{\partial M(z)}{\partial z} \right) |_{z=1}
\]
\[
\frac{d\eta_2}{dt} = \frac{d}{dt} \left( z \frac{\partial M(z)}{\partial z} \right) |_{z=1}
\]

Similar equations apply for the \( S_n \) distribution \((\lambda_{0,1,2})\). The differentiation becomes tedious, as the limit evaluation requires repeated use of L'Hopital's Rule, and is greatly facilitated by the use of a math software package, e.g. Mathematica. After simplifying, the moment equations are given by
\[
\frac{d\lambda_0}{dt} = k_6 [TT] \lambda_0
\]
\[
\frac{d\lambda_1}{dt} = \frac{k_1 T_p f_s}{2} (\eta_2 - \eta_1) + k_2 f_s \left[ \lambda_1 (\eta_1 - \eta_0) - \frac{\lambda_0}{2} (\eta_2 - \eta_1) \right]
\]
\[+k_3 f_s \lambda_1 \eta_1 + k_6 [TT] \lambda_1 + k_7 f_\nu \lambda_1 \eta_1
\]
\[
\frac{d\lambda_2}{dt} = \frac{k_1 T_p f_s}{6} (\eta_1 + 3 \eta_2 - 4 \eta_3) + k_3 f_s (2 \lambda_1 \eta_2 + \lambda_2 \eta_1)
\]
\[+k_2 f_s \left[ \lambda_2 (\eta_1 - \eta_0) + \lambda_1 (\eta_2 - \eta_1) - \frac{\lambda_0}{6} (4 \eta_3 - 3 \eta_2 + \eta_1) \right]
\]
\[+k_5 [TT] \lambda_2 + k_7 f_\nu (2 \lambda_1 \eta_2 + \lambda_2 \eta_1)
\]
\[
\frac{d\lambda_0}{dt} = k_1 T_p f_s (\eta_1 - \eta_0) - k_3 f_s \eta_1 \lambda_0 - k_6 [TT] \lambda_0 - k_7 f_\nu \eta_1 \lambda_0
\]
\[
\frac{d\lambda_1}{dt} = \frac{k_1 T_p f_s}{2} (\eta_2 - \eta_1) - k_2 f_s \left[ \lambda_1 (\eta_1 - \eta_0) - \frac{\lambda_0}{2} (\eta_2 - \eta_1) \right]
\]
\[-k_3 f_s \lambda_1 \eta_1 - k_6 [TT] \lambda_1 - k_7 f_\nu \lambda_1 \eta_1
\]
\[
\frac{d\lambda_2}{dt} = \frac{k_1 T_p f_s}{6} (2 \eta_3 - 3 \eta_2 + \eta_1) + \frac{k_2 f_s \lambda_0}{6} (2 \eta_3 - 3 \eta_2 + \eta_1)
\]
\[-k_2 f_s \lambda_2 (\eta_1 - \eta_0) - k_3 f_s \eta_1 \lambda_2 - k_6 [TT] \lambda_2 - k_7 f_\nu \eta_1 \lambda_2
\]
Given the extent of mathematical manipulation required to obtain the moment equations, a cursory check of the equations against the simplified mechanism (Table 4) is appropriate. First, the total number of mers is constant, i.e.

\[
\frac{d\eta_1}{dt} + \frac{d\lambda_1}{dt} = 0
\]

Second, \(\eta_0\), the total concentration of \(M_n\) chains, is increased by Reaction 6 only while \(\lambda_0\), the total concentration of \(S_n\) chains, is increased by Reaction 1, and decreased by Reactions 3, 6, and 7.

Lastly, consider the molecular weight effects predicted by the moment equations (Table 6). The effects were predicted by isolating the moment contributions from each reaction and applying the molecular weight definitions in Eqns. (3) and (4). As expected, Reaction 1 can only decrease \(MW\), Reactions 3 and 7 can only increase \(MW\), and Reaction 6 has no direct effect. Reaction 2, however, has no effect on \(MW_n\), but can either increase or decrease \(MW_w\) since

\[
\left(\frac{d\eta_2}{dt} + \frac{d\lambda_2}{dt}\right)_{Rxn2} = k_2 f_s \left[ \lambda_1 (\eta_2 - \eta_1) + \frac{\lambda_0}{3} (\eta_1 - \eta_2) \right]
\]

Consideration of these effects is useful when tuning model parameters.

Table 6: Predicted Qualitative \(MW\) Effects

<table>
<thead>
<tr>
<th>Rxn</th>
<th>(MW_w)</th>
<th>(MW_n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>↓</td>
<td>↓</td>
</tr>
<tr>
<td>2</td>
<td>↑↓</td>
<td>-</td>
</tr>
<tr>
<td>3,7</td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td>6</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

E. Model Summary and Solution Requirements

In summary, based on the simplified mechanism of Table 4, Model I predicts the polymer number and weight-average molecular weights, and the Thpidone, TETD, and reactive site concentrations versus aging time. It is comprised of the following 12, coupled ODEs:

\[
\frac{dT_w}{dt} = -\frac{k_m A_p}{V_w} \left[ T_w - \left( \frac{1}{PC} \right) T_p \right] 
\]  

(30)

\footnote{In application, only the first RHS term in Eqn (39) is retained and \(k_1 f_s\) is expanded to \([k_1 f_s + 2k_1,red(f_{so}-f_s)]\) in other rate expressions. A similar treatment is applied to \(k_2 f_s\).}
\[
\frac{dT_p}{dt} = \frac{k_m a_p}{v_p} \left[ T_w - \left( \frac{1}{PC} \right) T_p \right] - k_1 T_p f_s (\eta_1 - \eta_0) + k_6 [TT] \lambda_0
\] (31)

\[
\frac{d[TT]}{dt} = -k_6 [TT] \lambda_0
\] (32)

\[
\frac{d\eta_0}{dt} = k_6 [TT] \lambda_0
\] (33)

\[
\frac{d\eta_1}{dt} = -\frac{k_1 T_p f_s}{2} (\eta_2 - \eta_1) + k_2 f_s \left[ \lambda_1 (\eta_1 - \eta_0) - \frac{\lambda_0}{2} (\eta_2 - \eta_1) \right] + k_3 f_s \lambda_1 \eta_1 + k_6 [TT] \lambda_1 + k_7 f_s \lambda_1 \eta_1
\] (34)

\[
\frac{d\eta_2}{dt} = \frac{k_1 T_p f_s}{6} (\eta_1 + 3\eta_2 - 4\eta_0) + k_3 f_s (2\lambda_1 \eta_2 + \lambda_2 \eta_1) + k_2 f_s \left[ \lambda_2 (\eta_1 - \eta_0) + \lambda_1 (\eta_2 - \eta_1) - \frac{\lambda_0}{6} (4\eta_3 - 3\eta_2 + \eta_1) \right] + k_6 [TT] \lambda_2 + k_7 f_s (2\lambda_1 \eta_2 + \lambda_2 \eta_1)
\] (35)

\[
\frac{d\lambda_0}{dt} = k_1 T_p f_s (\eta_1 - \eta_0) - k_3 f_s \eta_1 \lambda_0 - k_6 [TT] \lambda_0 - k_7 f_\sigma \eta_1 \lambda_0
\] (36)

\[
\frac{d\lambda_1}{dt} = \frac{k_1 T_p f_s}{2} (\eta_2 - \eta_1) - k_2 f_s \left[ \lambda_1 (\eta_1 - \eta_0) - \frac{\lambda_0}{2} (\eta_2 - \eta_1) \right] - k_3 f_s \lambda_1 \eta_1 - k_6 [TT] \lambda_1 - k_7 f_\sigma \lambda_1 \eta_1
\] (37)

\[
\frac{d\lambda_2}{dt} = \frac{k_1 T_p f_s}{6} (2\eta_3 - 3\eta_2 + \eta_1) + \frac{k_2 f_s \lambda_0}{6} (2\eta_3 - 3\eta_2 + \eta_1) - k_2 f_s \lambda_2 (\eta_1 - \eta_0) - k_3 f_s \eta_1 \lambda_2 - k_6 [TT] \lambda_2 - k_7 f_\sigma \eta_1 \lambda_2
\] (38)

\[
\frac{d[RS]}{dt} = -k_1 T_p f_s (\eta_1 - \eta_0) + (k_3 f_s + k_7 f_\sigma) \eta_1 \lambda_0 + k_6 [TT] \lambda_0
\] (39)

\[
\frac{d[AC]}{dt} = -k_3 f_s \eta_1 \lambda_0
\] (40)

\[
\frac{d[VC]}{dt} = -k_7 f_\sigma \eta_1 \lambda_0
\] (41)

Supporting algebraic expressions include:

\[
\eta_3 = \frac{\eta_2 (2\eta_0 \eta_2 - \eta_1^2)}{\eta_0 \eta_1}
\]

\[
f_s = \frac{[RS]}{\eta_1 + \lambda_1}
\]

\[
a = \frac{[AC]}{\eta_1 + \lambda_1}
\]

\[
\sigma = \frac{[VC]}{\eta_1 + \lambda_1}
\]

\[
MW_a = w \left[ x_M \left( \frac{\eta_1}{\eta_0} \right) + x_a \left( \frac{\lambda_1}{\lambda_0} \right) \right]
\]
\[
MW_w = w \left[ x_M \left( \eta_2 \over \eta_1 \right) + x_S \left( \lambda_2 \over \lambda_1 \right) \right]
\]

\[
PD = MW_w / MW_n
\]

where \( w \) is the mer molecular weight and \( x_M \) and \( x_S \) are the weight fractions of the \( M_n \) and \( S_n \) populations, respectively. Simple algebraic equations, detailed in Appendix III, are also used to calculate initial conditions from user-supplied data. Specifically, the user specifies the unperturbed polymer MWD, the weight-average particle diameter, recipe variables, reaction rate constant parameters, and other physical constants. Sample data files are also included in Appendix III.

III. Simulation Development

A. Computer Strategy

The FORTRAN code used to solve Model I is charted in Figure 7 and detailed in Appendix III. The subroutine ALGBR reads the input data files (RCP1 and CNST1) and calculates the initial conditions for the ODEs, which are numerically integrated using Gear’s backward differentiation method. The IVPAG subroutine is available as part of the International Mathematical and Statistical Library (IMSL) software package. Results are written to three output files, MOLWGT, SITES, and MOMENT, examples of which are also included in Appendix III. The FORTRAN code is executed on a Digital Equipment Corporation VAX 6210.

B. Parameter Estimation

Most of the crucial model parameters were unavailable in the literature, and estimates were obtained from a kinetic study by S. Arthur[6]. The reader is referred to Reference [6] for experimental details and discussion, but rate constant estimates are presented in Table 7.

Assuming an Arrhenius dependence is applicable, i.e.

\[
k = Ae^{E \over RT}
\]

a plot of \( \ln k \) vs. \( \frac{1}{T} \) is characterized by a slope of \( -\frac{E}{R} \) and an intercept equal to \( \ln A \). Table 8 lists the calculated Arrhenius parameters, assuming \( k_1 \) and \( k_6 \) have the same temperature dependence, as do \( k_2 \) and \( k_3 \) (by assumption). In the absence of explicit data, these assumptions are made since Reactions 1 and 6 involve similar molecules, as do Reactions 2 and 3.

The rate constants reported in Table 7 were measured in both an 85:15 acetonitrile/water solution and methylene chloride, the polarity of which is thought to more closely resemble that of the particle. While potential
CALL ALGBR

Read input data files, calculate init. cond.

Adjust for:
- Allylic Cl isomer

CALL IVPAG

Solve ODEs

WRITE RESULTS?

YES

CALCULATE MW

WRITE RESULTS

NO

END SIMULATION?

YES

CLOSE OUTPUT FILES

STOP

Figure 7: Peptization Model Flowchart
Table 7: Rate Constant Estimates[6]

<table>
<thead>
<tr>
<th>Rate Constant</th>
<th>Value, l/mol - sec</th>
<th>Temp., °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃CN/H₂O</td>
<td>CH₂Cl₂</td>
<td></td>
</tr>
<tr>
<td>k₁</td>
<td>19</td>
<td>10⁻²⁻⁻¹⁴</td>
</tr>
<tr>
<td>k₁</td>
<td>49</td>
<td>—</td>
</tr>
<tr>
<td>k₂</td>
<td>76</td>
<td>—</td>
</tr>
<tr>
<td>k₃</td>
<td>0.19</td>
<td>10⁻²</td>
</tr>
<tr>
<td>k₃</td>
<td>0.49</td>
<td>—</td>
</tr>
<tr>
<td>k₆</td>
<td>60</td>
<td>10⁻¹⁻¹²</td>
</tr>
<tr>
<td>k₇</td>
<td>1.2×10⁻⁶</td>
<td>—</td>
</tr>
<tr>
<td>k₇</td>
<td>1.2×10⁻⁴</td>
<td>—</td>
</tr>
</tbody>
</table>

Table 8: Arrhenius Parameters

<table>
<thead>
<tr>
<th>(E/ₐK), K</th>
<th>A, cc/mol·sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>k₁</td>
<td>4866.</td>
</tr>
<tr>
<td>k₂</td>
<td>4594.</td>
</tr>
<tr>
<td>k₃</td>
<td>5169.</td>
</tr>
<tr>
<td>k₆</td>
<td>4603.</td>
</tr>
<tr>
<td>k₇</td>
<td>8498.</td>
</tr>
</tbody>
</table>
medium polarity effects appear significant, rate constant measurements using swollen and unswollen particles revealed an insensitivity of the rate of diffusion of small molecules (e.g., Tepidone, TETD) to the degree of swelling[6]. Thus, Reactions 1 and 6 are probably less affected by medium viscosity than are Reactions 2, 3, and 7, which involve two macromolecules. The model allows for independent adjustment of the constants for medium polarity and viscosity effects (RMEDCOR parameters).

Still another adjustment is made to \( k_3 \), the rate constant characterizing the branching reaction at the allylic chloride. Arthur[6] was unable to synthesize a pure sample of the tertiary allylic chloride, so the reported \( k_3 \) applies to the primary isomer. The respective rate constants may differ by 5X (tertiary more reactive). However, by the time 30% of the tertiary isomer has reacted, the remainder has rearranged to the primary isomer. Thus, Model I multiplies \( k_3 \) by 5 until 30% of the allylic chloride sites are branched, at which point the adjustment ceases.

The final rate constant adjustment is made to accommodate an apparent reduction in the reactivity of the polysulfide linkages as peptization progresses and the overall sulfur rank is reduced. This is consistent with the presence of residual cleavable sites in the peptized rubber. Arthur[6] quantified this reduction by measuring \( k_1 \) with di-, tri- and tetrasulfide in \( CH_3CN/H_2O \) at 22°C.

<table>
<thead>
<tr>
<th>Sulfur Rank</th>
<th>( k_1, l/mol \cdot sec )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>3.3E-04</td>
</tr>
<tr>
<td>3</td>
<td>6.4E-02</td>
</tr>
<tr>
<td>4</td>
<td>2.0E+01</td>
</tr>
</tbody>
</table>

By inference, \( k_1 \) for \( S_6 \) is probably on the order of \( 10^2 \), and is reduced by 2 or 3 orders of magnitude when \( S_6 \) is cleaved to a linkage of lower rank. In the model, \( k_1 \) and \( k_2 \) are multiplied by a user-specified reduction factor (RKRED) in rate expressions for lower sulfur rank linkages.

In addition to rate constant estimates, Arthur[6] also reports useful mass transfer-related data. The Tepidone partition coefficient is estimated at \( 1/150 \), and Tepidone uptake data (t vs. \( T_w \)) is reported for several Neoprene GRT latexes. Using this data, Schork[11] estimated \( k_m \), the mass transfer coefficient, at 6.4E-10 cm/sec.
IV. Simulation Results

A. Comparison with Laboratory Data

G Neoprene peptization sample sets, prepared and analyzed by Gossen and Aronson[3], were used to further improve the rate constant, and other model parameter, estimates. Experimental details are reported separately[3]; conditions are summarized in Table 9. Weight-averaged particle diameters were calculated from light transmission data according to \( D_p = 117 - 1.68(\% \text{trans}) \), as reported by Aronson[5]. The runs basically involved aging unstripped G Neoprene plant or miniworks latex samples under controlled laboratory conditions. With the exception of Run 3, the aging temperature was maintained at 40°C, but Tepidone and TETD concentrations were intentionally varied. Samples were analyzed for MWD (GPC in THF), residual TETD, Mooney viscosity, and various other data. Standard Neoprene GW and GRT recipes are presented in Appendix II, along with some analytical results for each of the six sample sets. Use of the data to improve model parameter estimates is presently discussed.

Table 9: Summary of Peptization Experiments[3]

<table>
<thead>
<tr>
<th>Run #</th>
<th>Polymer Type</th>
<th>Conv. %</th>
<th>( D_p ), nm</th>
<th>Sulfur, g phm</th>
<th>Pep. T, °C</th>
<th>TETD, g phm</th>
<th>Tepidone N, g phm</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Standard)</td>
<td>GRT</td>
<td>83-85</td>
<td>95-100</td>
<td>0.335</td>
<td>40</td>
<td>1.1800</td>
<td>2.0000</td>
</tr>
<tr>
<td>(Standard)</td>
<td>GWM2</td>
<td>71.3</td>
<td>90.1</td>
<td>0.335</td>
<td>40</td>
<td>1.1800</td>
<td>0.7976</td>
</tr>
<tr>
<td>1</td>
<td>GRTM2</td>
<td>84.7</td>
<td>93.5</td>
<td>0.600</td>
<td>30</td>
<td>0.4815</td>
<td>1.3607</td>
</tr>
<tr>
<td>2</td>
<td>GRT</td>
<td>82.2</td>
<td>—</td>
<td>0.600</td>
<td>40</td>
<td>0.4468</td>
<td>0.8505</td>
</tr>
<tr>
<td>3</td>
<td>GRT</td>
<td>84.7</td>
<td>93.5</td>
<td>0.600</td>
<td>30</td>
<td>0.4815</td>
<td>0.8505</td>
</tr>
<tr>
<td>4</td>
<td>GWM2</td>
<td>70.8</td>
<td>102</td>
<td>0.335</td>
<td>40</td>
<td>1.1800</td>
<td>2.1300</td>
</tr>
<tr>
<td>5</td>
<td>GRTM1</td>
<td>84.4</td>
<td>102</td>
<td>0.600</td>
<td>40</td>
<td>0.5519</td>
<td>2.2547</td>
</tr>
</tbody>
</table>

*2nd shot added after 24 hrs = 1.3015.

Molecular weight profiles of the laboratory sample sets are shown in Figure 8 (data in Table A.II.1). To aid discussion, the peptization reactions, rate constant order of magnitudes, and probable correction factors are summarized in Table 10. In Table 10, the reaction rate order of magnitude (from Table 7) is multiplied by factors estimating the difference between the polarity and viscosity of acetonitrile/water and the particle interior. A sulfur rank adjustment is also included because \( k_1 \) and \( k_2 \) were measured using an \( S_6 \) model compound[6], and the more reactive \( S_6 \) is presumed prevalent in the unpeptized polymer.
Figure 8: GW and GRT Experimental $MW_w$ Profiles[3].
Table 10: Peptization Rate Constants

<table>
<thead>
<tr>
<th>Peptization Reaction</th>
<th>$k_i$, cc/mol-sec (in CH$_3$CN/H$_2$O, 20°C)</th>
<th>Rate Adjustments</th>
<th>Polarity</th>
<th>Visc</th>
<th>S Rank</th>
<th>$k_i$, cc/mol-sec (in particle, 20°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_n + T^- \xrightarrow{k_i} S^-M_q + M_{n-q}T$</td>
<td>$O(10^4)$</td>
<td></td>
<td>$10^{-3}$-$10^{-5}$</td>
<td>1</td>
<td>10</td>
<td>$O(1-10^2)$</td>
</tr>
<tr>
<td>$M_n + S^-M_q \xrightarrow{k_i} M_r + S^-M_m$</td>
<td>$O(10^4)$</td>
<td></td>
<td>$10^{-3}$-$10^{-5}$</td>
<td>$10^{-1}$</td>
<td>10</td>
<td>$O(10^{-1}-10)$</td>
</tr>
<tr>
<td>$M_n + S^-M_q \xrightarrow{k_i} M_{n+q} + Cl^-$</td>
<td>$O(10^2)$</td>
<td></td>
<td>$10^{-1}$</td>
<td>$10^{-1}$</td>
<td>1</td>
<td>$O(1)$</td>
</tr>
<tr>
<td>$TT + S^-M_q \xrightarrow{k_i} T^- + TSM_q$</td>
<td>$O(10^4)$</td>
<td></td>
<td>$1-10$</td>
<td>1</td>
<td>1</td>
<td>$O(10^4-10^5)$</td>
</tr>
<tr>
<td>$M_n + S^-M_q \xrightarrow{k_i} M_{n+q} + Cl^-$</td>
<td>$O(10^{-3})$</td>
<td></td>
<td>$10^{-1}$</td>
<td>$10^{-1}$</td>
<td>1</td>
<td>$O(10^{-5})$</td>
</tr>
</tbody>
</table>
The corrected constants suggest that 1) reaction at the vinyl chloride sites (Reaction 7) is relatively insignificant, and 2) the reaction of TETD with polymeric sulfide ions is very fast. The potential dominance of Reaction 6 is of particular importance since this capping reaction is thought to deter MW increases. Note, however, that the rate of the branching (MW-increasing) and capping reactions are obviously also dependent upon the allylic Cl and TETD concentrations. At the beginning of a standard GRT peptization, the allylic Cl site concentration is roughly 3 orders of magnitude greater than the TETD concentration (calculated from the recipe in Appendix II). Therefore, as peptization continues, concentration differences could offset the disparity in rate constants, allowing a MW increase. This is possibly the case in Runs 4 and 6, where residual TETD is present (by titration), but the MW eventually increases.

Runs 4 and 6 do not, however, exhibit the large MW increases during the early stages of peptization observed in the Run 1, 2 and 3 sample sets. As discussed earlier (Section II.A.), the extent of this increase appears to be related to the unpeptized polymer structure[3]. Polymer characterized by a persistent multimodal MWD with a preponderance of low MW chains exhibit a larger, more sustained MW increase during the early stages of peptization (Runs 1, 2, and 3). Model I does not accommodate multimodal MWDs and therefore does not predict this early MW increase. Similarly, several sample sets exhibited a significant change in MW with the addition of TETD only (Table 3). The Model I mechanism requires Tepidone for the onset of peptization, but is still useful if a continued MW increase does not ensue. Run 4 simulations are presented first.

In Run 4, the standard recipe TETD and Tepidone charges are decreased by 20% and doubled, respectively, to force an increase in Mooney viscosity with peptization time. Simulations are shown in Figures 9 and 10. Rate constant correction factors are summarized in Table 11 (k7 is omitted, but was adjusted in the same manner as k3). The required corrections for k1, k2, and k3 were in the expected ranges, but k6 was reduced further to obtain a reasonable fit to the Mw data (Figure 9a). This is consistent with the substantial (~50%) residual TETD level (Figures 9b and 10a). With a very high k6, the MW continued to decrease despite the high allylic Cl concentration (Figure 10b). The residual aqueous-phase Tepidone concentration is also substantial (~60%, Figure 10a), and the particle-phase concentration is relatively low (Figure 10c). This aqueous phase preference is consistent with the estimated Tepidone partition coefficient[6]. Returning to Figure 10b, note that the more reactive S6 linkage level is plotted. As these are cleaved, less reactive sites remain. Polydispersities (not shown) were higher than expected, possibly reflecting the unimodal MWD assumption or the need for further k2 adjustment.
Table 11: Rate Constant Correction Factors

<table>
<thead>
<tr>
<th>Constant</th>
<th>Run 4</th>
<th>Run 6</th>
<th>Run 2</th>
<th>Run 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1$</td>
<td>4.00E-02</td>
<td>3.00E-02</td>
<td>3.00E-02</td>
<td>3.00E-02</td>
</tr>
<tr>
<td>$k_2$</td>
<td>3.00E-03</td>
<td>3.00E-03</td>
<td>3.00E-03</td>
<td>3.00E-03</td>
</tr>
<tr>
<td>$k_3$</td>
<td>3.15E-02</td>
<td>3.30E-02</td>
<td>3.30E-02</td>
<td>8.75E-02</td>
</tr>
<tr>
<td>$k_4$</td>
<td>2.50E-03</td>
<td>2.00E-03</td>
<td>2.00E-03</td>
<td>2.00E-03</td>
</tr>
</tbody>
</table>

Figure 9: Model Fit to Run 4 $MW_w$ and wt% TETD.
Figure 10: $T_w$, TETD, Reactive Site and $T_p$ Predictions (Run 4)
Run 6 tracked a 'GRTM1' (a GW Tepidone charge was inadvertently added) peptization over 3 days. Additionally, a second TETD shot was added to some samples after 24 hours. Simulations are shown in Figures 11 and 12. With only slight adjustment of the rate constants used for Run 4 simulations (Table 11), a reasonable $MW_w$ fit is obtained (Figure 11a) and an impressive wt% TETD prediction is noted (Figure 11b). Consistent with the proposed reaction mechanism, the second TETD shot reverses the MW increase by capping chains that would otherwise be coupled. Figure 12 shows the expected decrease in the rate of allylic Cl depletion.

Figure 11: Model Fit to Run 6 $MW_w$ and wt% TETD.
In Run 2, a standard GRT peptization, $MW_w$ doubled during the first hour of peptization, presumably reflecting polymer structural changes associated with the transition from a multimodal to unimodal MWD. Model I does not accommodate these changes, but simulation of the subsequent $MW_w$ decrease is shown in Figure 13. Here, the aged polymer properties were used as initial conditions. The initial Tepidone and TETD concentrations were not adjusted since $T_p$ quickly assumes a low value, and a substantial TETD residual was measured. Allylic Cl and polysulfide site concentrations were likewise unadjusted since the structural reconfiguration chemistry has not been identified.
Lastly, Run 5 tracked a standard GW peptization for 3 hours. While the unpeptized polymer MWD was not perfectly unimodal, $MW_n$ was not extremely low and a smooth $MW_w$ decrease was measured. A good fit of the data was obtained (Figure 14a) by more than doubling $k_3$, the rate constant for branching at the allylic Cl (Table 11). A corresponding increased allylic Cl depletion is not predicted (Figure 14b). The correctness of this $k_3$ increase should be weighed in light of GW and GRT polymer differences.

![Figure 14: Model Fit to Run 5 $MW_w$, Allylic Cl Prediction.](image)
B. Sensitivity Analysis

The sensitivity of Model I predictions to the reaction rate constants ($k_1$, $k_2$, $k_3$, $k_6$), recipe parameters (Tepidone, TETD, sulfur incorporation), the rate reduction factor, and mass transfer parameters (Tepidone partition coefficient, $k_m$, $D_p$) is evaluated by changing the subject parameter, while leaving the others unchanged. (Alternatively, one might employ a rigorous statistical procedure, e.g. ANOVA, for further detail.) The standard GRT recipe, with Run 4 rate constant correction factors, is used as the base condition.

Sensitivity of the $MW_\infty$ predictions to ±50% changes in $k_1$ and Tepidone concentration is shown in Figure 15. Consistent with Reaction 1, increasing $k_1$ or the Tepidone concentration increases the rate at which polysulfide linkages are cleaved, and thus the $MW_\infty$ reduction rate. Since this is a rate effect, a comparable MW is reached, sooner or later, in all cases. However, acceleration or deceleration of this rate similarly affects the onset of an observable MW increase due to branching.

![Figure 15: Model Sensitivity to $k_1$ and [Tepidone].](image-url)
With fixed rate constants, the minimum predicted MW varies with sulfur incorporation (Figure 16). Although not verified quantitatively, the scale of this variance appears consistent with incorporated sulfur versus Mooney viscosity data reported by Aronson\cite{5}. Less incorporated sulfur results in fewer polysulfide linkages, the cleavable sites affording MW reduction, and higher final MW levels.

![Figure 16: Model Sensitivity to Sulfur Incorporation.](image)

Figure 16: Model Sensitivity to Sulfur Incorporation.
MW profiles are also sensitive to $k_3$ and $k_6$, the rate constants governing the branching (allylic Cl) and capping reactions. As shown in Figure 17, and explained by the proposed mechanism, increasing $k_3$ increases the likelihood that a polymeric sulfide ion will be branched via Reaction 3, rather than redistributed (Reaction 2) or capped (Reaction 6). Note that MW does not increase when $k_3$ and TETD are increased simultaneously (Figure 17a). However, the MW increase is accelerated with significant decreases in either $k_6$ or TETD (Figure 17b) since polymer chains are again more likely to be branched than capped.

Figure 17: Model Sensitivity to $k_3$, $k_6$ and [TETD].
Consistent with the proposed mechanism, adjusting $k_2$, the rate constant characterizing the MW redistribution reaction, appears to affect the final MW attained, but not the MW reduction rate (Figure 18). Increased redistribution appears to lower both the $MW_w$ and polydispersity. This is noted in light of the model equations, which suggest that Reaction 2 can decrease or increase MW depending on the polymer chain ($M_n$) and polymeric sulfide ion ($S_n$) distributions (Section II.D.). The polydispersity profile is unexpected and may reflect the unimodal MWD assumption.

Figure 18: Model Sensitivity to $k_2$. 
Both $k_2$ and $k_1$ are corrected for the continued reduction of $S_6$ linkages to $S_2$, $S_3$ and/or $S_4$ sites, whose reactivity is reduced by at least 2 to 3 orders of magnitude. Adjusting this parameter (RKRED, from base $10^{-2}$ and $10^{-3}$) does not significantly affect the early aging curve, when $S_6$ sites are relatively plentiful. However, when the $S_6$ sites are nearly depleted, decreasing RKRED can virtually halt all reactions in the Model I mechanism. Specifically, if Reaction 1 does not proceed, the polymeric sulfide ions ($S_n$) required for Reactions 2, 3 and 6 are not formed, and all reactions cease. This is depicted in Figure 19, where the MW increase observed during Run 6 is not predicted if RKRED is reduced by an order of magnitude (to $10^{-3}$).

![Figure 19: Model Sensitivity to RKRED.](image)

Lastly, consider model sensitivity to mass transfer parameters. Of the three parameters considered (Tepidone partition coefficient, $k_m$, and $D_p$), only the particle diameter does not significantly affect the peptization rate. The Tepidone partition coefficient (PC) was estimated at $\frac{1}{150}$ [6], but could be as low as $\frac{1}{1000}$ or as high as $\frac{1}{10}$ [11]. As shown in Figure 20a, decreasing PC by an order of magnitude decreases $T_p$ by roughly 90%, and lowers the peptization rate (Figure 20b). On the other hand, increasing PC by an order of magnitude accelerates the process to the extent that an early MW increase (due to branching) is observed. TETD depletion is accelerated (Figure 20c), with an ensuing reduction in the capping reaction rate.
Figure 20: Model Sensitivity to Tepidone Partition Coefficient (PC).
Order of magnitude changes in $k_m$, the mass transfer coefficient, significantly affect peptization, but ±20% changes in $D_p$, the weight-averaged particle diameter, do not significantly affect Tepidone transfer (Figure 21). A smaller particle and/or larger $k_m$ increases $T_p$ and thus accelerates the MW reduction, and vice versa, but, in the case of $D_p$, these effects are negligible. Thus, the increase in Mooney viscosity with particle size observed in practice is not fully explained by Tepidone mass transfer. Note, however, that changing either $k_m$ or $D_p$ by an order of magnitude has the same effect on $T_p$ predictions (Eqn. (20), $\frac{\Delta m}{m_D} = \frac{k_m}{D_p}$ for spherical particles). Thus the predicted particle size effect could be more significant for very polydisperse latexes.

Figure 21: Model Sensitivity to $k_m$ and $D_p$. 
C. Predictive Capability

Doyle's study of Mooney viscosity for Neoprene G types[7] provides useful data for independent assessment of the model predictive capability. Doyle measured aging curves (Mooney viscosity versus time) at 25°C for a wide range of TETD and Tepidone concentrations. While Mooney viscosity is not totally indicative of MWD (Figure 22), a general correlation appears valid (Figure 23), and was used to convert Doyle's aging curves to approximate $MW_w$ profiles. In the simulations that follow, the unpeptized polymer is assumed similar to that of Run 6, as are the rate constants.

Figure 24 shows the effect of varying the Tepidone level at a fixed TETD concentration. As expected, Mooney viscosity and $MW_w$ decrease with increased Tepidone concentration according to Reaction 1. Consistent with Reaction 6, at a fixed Tepidone level, $MW_w$ decreases with increased TETD concentration (Figure 25), as more chains are capped rather than branched. Mechanistically, fixing the TETD/Tepidone ratio balances the capping (and thus branching) and scission reactions.

Finally, in Figure 26, both the model predictions and experimental aging curves exhibit the expected increase in peptization rate with increased temperature. This is consistent with the representation of the rate constants by Arrhenius' law.
Figure 22: Mooney Curve.

Figure 23: Mooney/MW Correlation.
Figure 24: Model Comparison with Mooney Trends[7]: Constant TETD, Vary T−.
Figure 25: Model Comparison with Mooney Trends[7]: Constant $T^-$, Vary TETD.
Figure 26: Model Comparison with Mooney Trends[7]: Temperature Effect.
References


APPENDIX I
Nomenclature

\( \alpha_p \) surface area of a particle, \( \text{cm}^2/\text{particle} \)
\( A_p \) total surface area of particles, \( \text{cm}^2/\text{particle} \)
\([AC]\) allylic chloride concentration, \( \text{moles/cc - part} \)
\( f_a \) fraction allylic chlorides in polymer chain, \( \text{moles/mole mer} \)
\( f_s \) fraction polysulfide linkages in polymer chain, \( \text{moles/mole mer} \)
\( f_v \) fraction vinyl chlorides in polymer chain, \( \text{moles/mole mer} \)
\( k_i \) rate constant for Reaction \( i \), \( \text{cc/mole sec} \)
\( k_m \) mass transfer coefficient, \( \text{cm/sec} \)
\( M_n \) polymer of chain length \( n \), \( \text{moles/cc - part} \)
\( MW_n \) number-average molecular weight, \( \text{g/mole} \)
\( MW_w \) weight-average molecular weight, \( \text{g/mole} \)
\([RS]\) polysulfide reactive site concentration, \( \text{moles/cc - part} \)
\( S-M_n,S_n \) polymeric sulfide ion of chain length \( n \), \( \text{moles/cc - part} \)
\( T^- \) dithiocarbamate (ethyl or butyl), \( \text{moles/cc} \)
\( T_p \) Tepidone in particle, \( \text{moles/cc - part} \)
\( T_w \) Tepidone in aqueous phase \( \text{moles/cc - aq} \)
\( TETD,T_eT_e \) tetraethylthiuram disulfide, \( \text{moles/cc - part} \)
\( TeT_b \) tetra \( n \)-butyl thiuram disulfide
\( T_eT_b \) diethylidibutylthiuram disulfide
\( TT \) thiuram disulfide (ethyl, butyl, or mixed), \( \text{moles/cc - part} \)
\( v_p \) volume of a particle, \( \text{cc/particle} \)
\([VC]\) vinyl chloride concentration, \( \text{moles/cc - part} \)
\( V_w \) aqueous-phase volume, \( \text{cc - aq} \)
\( w \) monomer molecular weight, \( \text{g/mole} \)

\( M(z) \) \( \text{z-transform of } M_n \)
\( S(z) \) \( \text{z-transform of } S_n \)
\( \eta_i \) \( i \text{th moment of } M_n \text{ distribution} \)
\( \lambda_i \) \( i \text{th moment of } S_n \text{ distribution} \)

\(^1\text{See Appendix III for computer variable notation.}\)
## APPENDIX II

**Neoprene GW Recipe**

<table>
<thead>
<tr>
<th><strong>Monomer Solution</strong></th>
<th>parts per 100 Monomer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroprene</td>
<td>100.0</td>
</tr>
<tr>
<td>Rosin S</td>
<td>4.0</td>
</tr>
</tbody>
</table>

**Water Solution**
- Demineralized water: 93.97
- Copper Ion: 0.4 ppm
- Sodium Hydroxide (50%): 1.26
- Sodium Chloride: 0.075

**Sulfur Dispersion**
- Sulfur: 0.335
- 20% 'Lomar' PW: 1.75

**Catalyst Solution (A-3)**
- Demineralized water: 1.613
- Potassium persulfate: 0.085
- Silver salt: 0.0021

**Kettle Stabilizer (Type V)**
- Toluene: 1.634
- Demineralized water: 1.227
- Dresinate X: 0.034
- TETD: 1.180
- 'Ethyl' Antioxidant 736: 0.047
- 'Duponol' WAQE: 0.167

**Kettle Plasticizer**
- 'Tepidone' N: 2.0
- 'Duponol' WAQE: 0.13

**Model Parameters**
- DPART: 1.1206
- GTEPN: 2.00
- GTETD: 1.180
- GSUL: 0.335
- VW: 101.8
- WP: 107.71
Neoprene GRT Recipe

<table>
<thead>
<tr>
<th>Monomer Solution</th>
<th>parts per 100 Monomer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroprene</td>
<td>98.0</td>
</tr>
<tr>
<td>ACR</td>
<td>2.0</td>
</tr>
<tr>
<td>Rosin S</td>
<td>4.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Water Solution</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Demineralized water</td>
<td>105.77</td>
</tr>
<tr>
<td>Copper Ion</td>
<td>0.4 ppm</td>
</tr>
<tr>
<td>Sodium Hydroxide(50%)</td>
<td>1.40</td>
</tr>
<tr>
<td>Sodium Chloride</td>
<td>0.075</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sulfur Dispersion</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur</td>
<td>0.6</td>
</tr>
<tr>
<td>20% 'Lomar' PW</td>
<td>3.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Catalyst Solution (A-3)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Demineralized water</td>
<td>4.270</td>
</tr>
<tr>
<td>Potassium persulfate</td>
<td>0.225</td>
</tr>
<tr>
<td>Silver salt</td>
<td>0.0056</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Kettle Stabilizer (Type I)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>0.6325</td>
</tr>
<tr>
<td>Demineralized water</td>
<td>0.6031</td>
</tr>
<tr>
<td>Dresinate X</td>
<td>0.0150</td>
</tr>
<tr>
<td>TETD</td>
<td>0.4348</td>
</tr>
<tr>
<td>Santowhite Crystals</td>
<td>0.0925</td>
</tr>
<tr>
<td>'Duponol' WAQE</td>
<td>0.0721</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Kettle Plasticizer</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>'Tepidone' N</td>
<td>0.799</td>
</tr>
<tr>
<td>'Duponol' WAQE</td>
<td>0.051</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Model Parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>DPART</td>
<td>1.1603</td>
</tr>
<tr>
<td>GTEPN</td>
<td>0.799</td>
</tr>
<tr>
<td>GTETD</td>
<td>0.4348</td>
</tr>
<tr>
<td>GSUL</td>
<td>0.6</td>
</tr>
<tr>
<td>VW</td>
<td>115.33</td>
</tr>
<tr>
<td>WP</td>
<td>106.64</td>
</tr>
</tbody>
</table>
Table 12: Laboratory Peptization Sample Data*[3]

<table>
<thead>
<tr>
<th>Aging Time</th>
<th>$MW_n$</th>
<th>$MW_w$</th>
<th>PD</th>
<th>TETD, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run 1 (GWM2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>before $T^-$, TETD</td>
<td>184,000</td>
<td>1,736,000</td>
<td>9.4</td>
<td>—</td>
</tr>
<tr>
<td>10 min.</td>
<td>136,000</td>
<td>2,459,000</td>
<td>18.1</td>
<td>—</td>
</tr>
<tr>
<td>30 min.</td>
<td>184,000</td>
<td>2,415,000</td>
<td>11.0</td>
<td>—</td>
</tr>
<tr>
<td>105 min.</td>
<td>171,000</td>
<td>2,158,000</td>
<td>12.6</td>
<td>—</td>
</tr>
<tr>
<td>Run 2 (GRT)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>before $T^-$, TETD</td>
<td>108,000</td>
<td>854,000</td>
<td>7.9</td>
<td>0.10</td>
</tr>
<tr>
<td>after TETD, before $T^-$</td>
<td>105,000</td>
<td>1,408,000</td>
<td>13.4</td>
<td>0.26</td>
</tr>
<tr>
<td>30 min.</td>
<td>104,000</td>
<td>1,269,000</td>
<td>12.2</td>
<td>0.35</td>
</tr>
<tr>
<td>45 min.</td>
<td>108,000</td>
<td>1,441,000</td>
<td>13.4</td>
<td>0.31</td>
</tr>
<tr>
<td>60 min.</td>
<td>121,000</td>
<td>2,143,000</td>
<td>17.7</td>
<td>0.26</td>
</tr>
<tr>
<td>1.25 hr</td>
<td>128,000</td>
<td>2,141,000</td>
<td>16.7</td>
<td>0.26</td>
</tr>
<tr>
<td>2.00 hr</td>
<td>96,000</td>
<td>891,000</td>
<td>9.3</td>
<td>0.29</td>
</tr>
<tr>
<td>5.00 hr</td>
<td>100,000</td>
<td>815,000</td>
<td>8.1</td>
<td>0.25</td>
</tr>
<tr>
<td>11.00 hr</td>
<td>102,000</td>
<td>865,000</td>
<td>8.5</td>
<td>0.18</td>
</tr>
<tr>
<td>Run 3 (GRT)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 min.</td>
<td>24,000</td>
<td>331,000</td>
<td>13.9</td>
<td>—</td>
</tr>
<tr>
<td>30 min.</td>
<td>66,000</td>
<td>932,000</td>
<td>14.1</td>
<td>—</td>
</tr>
<tr>
<td>3 hr</td>
<td>159,000</td>
<td>3,191,000</td>
<td>20.0</td>
<td>—</td>
</tr>
<tr>
<td>41.75 hr</td>
<td>118,000</td>
<td>774,000</td>
<td>6.5</td>
<td>—</td>
</tr>
<tr>
<td>Run 4 (GRTM2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>before $T^-$, TETD</td>
<td>109,000</td>
<td>1,119,000</td>
<td>10.3</td>
<td>—</td>
</tr>
<tr>
<td>after TETD, before $T^-$</td>
<td>—</td>
<td>1,516,000</td>
<td>—</td>
<td>0.29</td>
</tr>
<tr>
<td>0 hr</td>
<td>91,000</td>
<td>780,000</td>
<td>8.6</td>
<td>0.25</td>
</tr>
<tr>
<td>1 hr</td>
<td>116,000</td>
<td>579,000</td>
<td>5.0</td>
<td>0.25</td>
</tr>
<tr>
<td>2 hr</td>
<td>—</td>
<td>587,000</td>
<td>—</td>
<td>0.26</td>
</tr>
<tr>
<td>3 hr</td>
<td>—</td>
<td>638,000</td>
<td>—</td>
<td>0.24</td>
</tr>
<tr>
<td>4 hr</td>
<td>—</td>
<td>735,000</td>
<td>—</td>
<td>0.20</td>
</tr>
<tr>
<td>6 hr</td>
<td>—</td>
<td>985,000</td>
<td>—</td>
<td>0.23</td>
</tr>
<tr>
<td>10 hr</td>
<td>103,000</td>
<td>1,000,000</td>
<td>9.8</td>
<td>0.24</td>
</tr>
<tr>
<td>Run 5 (GWM2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>before $T^-$, TETD</td>
<td>236,000</td>
<td>1,844,000</td>
<td>7.8</td>
<td>0</td>
</tr>
<tr>
<td>30 min.</td>
<td>142,000</td>
<td>1,011,000</td>
<td>7.1</td>
<td>1.24</td>
</tr>
<tr>
<td>3 hr</td>
<td>136,000</td>
<td>861,000</td>
<td>6.3</td>
<td>1.24</td>
</tr>
<tr>
<td>Run 6 (GRTM1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>before $T^-$, TETD</td>
<td>105,000</td>
<td>1,579,000</td>
<td>15.0</td>
<td>0</td>
</tr>
<tr>
<td>after TETD, before $T^-$</td>
<td>114,000</td>
<td>625,000</td>
<td>5.5</td>
<td>0.55</td>
</tr>
<tr>
<td>0 hr</td>
<td>106,000</td>
<td>664,000</td>
<td>6.3</td>
<td>0.61</td>
</tr>
<tr>
<td>0.5 hr</td>
<td>102,000</td>
<td>495,000</td>
<td>4.9</td>
<td>0.61</td>
</tr>
<tr>
<td>20 hr</td>
<td>84,000</td>
<td>495,000</td>
<td>5.9</td>
<td>0.33</td>
</tr>
<tr>
<td>44 hr</td>
<td>89,000</td>
<td>1,001,000</td>
<td>11.2</td>
<td>0.30</td>
</tr>
<tr>
<td>49 hr</td>
<td>99,000</td>
<td>866,000</td>
<td>8.7</td>
<td>0.33</td>
</tr>
<tr>
<td>24.5 hr w/2nd TT</td>
<td>—</td>
<td>421,000</td>
<td>—</td>
<td>1.02</td>
</tr>
<tr>
<td>44 hr w/2nd TT</td>
<td>79,000</td>
<td>344,000</td>
<td>4.4</td>
<td>1.49</td>
</tr>
<tr>
<td>49 hr w/2nd TT</td>
<td>71,000</td>
<td>336,000</td>
<td>4.7</td>
<td>1.32</td>
</tr>
</tbody>
</table>
* $MW$ measured by GPC(THF), TT measured by titration.
### Appendix III

**Computer Program**

#### A. Variable Notation (underlined variables are required input)

<table>
<thead>
<tr>
<th>Variable</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A(1,1)</td>
<td>IVPAG parameter</td>
</tr>
<tr>
<td>Ai</td>
<td>frequency factor (Arrhenius' law) for RKi, ( cc/mole \text{ sec} )</td>
</tr>
<tr>
<td>AP</td>
<td>total surface area of particles, ( cm^2 ) - part</td>
</tr>
<tr>
<td>ALGBR</td>
<td>subroutine used to calculate initial conditions</td>
</tr>
<tr>
<td>CNST1.DAT</td>
<td>input data file</td>
</tr>
<tr>
<td>DCM</td>
<td>weight-average particle diameter, ( cm )</td>
</tr>
<tr>
<td>IVPAG</td>
<td>IMSL subroutine used to solve ODES</td>
</tr>
<tr>
<td>DNM</td>
<td>weight-average particle diameter, ( nm )</td>
</tr>
<tr>
<td>DPART</td>
<td>particle-phase density, ( g/cc ) - part</td>
</tr>
<tr>
<td>DY(i)</td>
<td>( Y(i) ) dummy used to facilitate data transfer</td>
</tr>
<tr>
<td>ERi</td>
<td>( E/R ) (Arrhenius' law) for RKi, ( K )</td>
</tr>
<tr>
<td>ETAi</td>
<td>( ith ) moment of ( M_n ) distribution, ( moles/cc ) - part</td>
</tr>
<tr>
<td>ETAij</td>
<td>contribution of ( jth ) reaction to ETAi, ( moles/cc ) - part ( sec )</td>
</tr>
<tr>
<td>FA</td>
<td>fraction allylic chlorides in polymer chain, ( mole/mole ) mer</td>
</tr>
<tr>
<td>FAQ</td>
<td>initial fraction allylic chlorides in polymer chain, ( mole/mole ) mer</td>
</tr>
<tr>
<td>FCN</td>
<td>IVPAG subroutine containing ODES</td>
</tr>
<tr>
<td>FCNJ</td>
<td>IVPAG subroutine containing dummy Jacobian</td>
</tr>
<tr>
<td>FCONV</td>
<td>fractional conversion at begin peptization</td>
</tr>
<tr>
<td>FETA</td>
<td>weight fraction ( M_n )</td>
</tr>
<tr>
<td>FLAM</td>
<td>weight fraction ( S_n )</td>
</tr>
<tr>
<td>FS</td>
<td>fraction polysulfide linkages in polymer chain, ( mole/mole ) mer</td>
</tr>
<tr>
<td>FSO</td>
<td>initial fraction polysulfide linkages in polymer chain, ( mole/mole ) mer</td>
</tr>
<tr>
<td>FSULINC</td>
<td>fraction recipe sulfur incorporated in polymer</td>
</tr>
<tr>
<td>FV</td>
<td>fraction vinyl chlorides in polymer chain, ( mole/mole ) mer</td>
</tr>
<tr>
<td>FVO</td>
<td>initial fraction vinyl chlorides in polymer chain, ( mole/mole ) mer</td>
</tr>
<tr>
<td>GSUL</td>
<td>sulfur, ( g ) phm</td>
</tr>
<tr>
<td>GSULINC</td>
<td>sulfur incorporated, ( g ) phm</td>
</tr>
<tr>
<td>GTEPN</td>
<td>Tepidone N, ( g ) phm</td>
</tr>
<tr>
<td>GTETD</td>
<td>TETD, ( g ) phm</td>
</tr>
<tr>
<td>H</td>
<td>IVPAG parameter</td>
</tr>
<tr>
<td>ICOUNT</td>
<td>count for write to output data files</td>
</tr>
<tr>
<td>IFLAG</td>
<td>flag to adjust RK3</td>
</tr>
<tr>
<td>INDEX</td>
<td>IVPAG parameter</td>
</tr>
</tbody>
</table>
INORM: IVPAG parameter
LAMi: $i$th moment of $S_n$ distribution, moles/cc — part
MEND: number of times IVPAG called
METH: IVPAG parameter
MOLWGT.DAT: output data file
MOMENT.DAT: output data file
MXSTEP: IVPAG parameter
NODES: IVPAG parameter
PARAM(50): IVPAG parameter
PCOUNT: write to output data files when ICOUNT=PCOUNT
RCP1.DAT: input data file
RKi: reaction rate constant for Reaction i, cc/mole sec
RKM: mass transfer coefficient, cm/sec
RKRED: factor by which RKi is reduced with S rank
RLAMij: contribution of $j$th reaction to RLAMi, moles/cc — part sec
RMEDCORi: medium polarity/viscosity correction factor
RMERMW: modified mer (chloroprene-sulfur) molecular weight, g/mole
RMN: $MW_n$ of unpeptized polymer, g/mole
RMONMW: monomer molecular weight, g/mole
RMW: $MW_w$ of unpeptized polymer, g/mole
RMWN: number-average molecular weight, g/mole
RMWWW: weight-average molecular weight, g/mole
RN: particle number
RPC: Tepidone partition coefficient, $(T_p/T_w)_{eq}$
RPCOUNT: PCOUNT (real)
RPD: polydispersity of MWD
RPI: $\pi$
SAP: surface area of particle, cm$^2$/particle
SIMTIM: simulation time, hrs
SITES.DAT: output data file
STEPN: Tepidone N step, g phm
STETD: TETD step, g phm
SULMW: sulfur molecular weight, g/mole
SVP: volume of particle, cc/particle
T: time, sec
TEMP: temperature, K
TEPMW: Tepidone molecular weight, g/mole
TETDMW: TETD molecular weight, g/mole
TIDG: IVPAG parameter
TIEND: IVPAG parameter
TOL: IVPAG parameter
TSTEP: ODEs solved every TSTEP seconds during SIMTIM
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>TWO</td>
<td>initial aqueous-phase Tepidone concentration, mole/cc - aq</td>
</tr>
<tr>
<td>VP</td>
<td>particle-phase volume, cc - part phm</td>
</tr>
<tr>
<td>VW</td>
<td>aqueous-phase volume, cc - aq phm</td>
</tr>
<tr>
<td>WP</td>
<td>particle-phase weight, g - part phm</td>
</tr>
<tr>
<td>WTETD</td>
<td>wt% TETD (based on dry polymer)</td>
</tr>
<tr>
<td>Y(i)</td>
<td>dependent variable for ith ODE, mole/sec</td>
</tr>
</tbody>
</table>

Note: 1-\( T_w \), 2-\( T_p \), 3-\( TT \), 4-\( \eta_0 \), 5-\( \eta_1 \), 6-\( \eta_2 \), 7-\( \lambda_0 \), 8-\( \lambda_1 \), 9-\( \lambda_2 \), 10-\([RS]\), 11-\([AC]\), 12-\([VC]\) |

| YPRIME(i) | right-hand-side of ODE for Y(i) |
B. Program Listing

PROGRAM PEP

C THIS PROGRAM SOLVES MODEL I FOR G-TYPE NEOPRENE ALKALINE AGING. C IT PREDICTS MOLECULAR WEIGHT, RESIDUAL REACTIVE SITES, AND C PEPTIZING AGENT CONCENTRATIONS VS AGING TIME.

C DECLARE STORAGE

DIMENSION A(1,1),PARAM(50),Y(12),DY(12)
EXTERNAL FCN,FCNJ,IVPAG

COMMON/MISC/ ETA3,DY,PCOUNT,RMERMW,SIMTIM,TSTEP,TWO,TTO
COMMON/PART/ AP,RKM,RPC,SAP,SVP,VW
COMMON/RKS/ RK1,RK2,RK3,RK6,RK7,RKRED
COMMON/SITES/ FS,FA,FV,FSO,FAO,FVO
COMMON/STEP/ T,TETDMW,TEPMW,VP,STETD,STEPN

C OPEN OUTPUT FILES

OPEN(UNIT=13,NAME='MOLWGT.DAT',TYPE='NEW')
OPEN(UNIT=14,NAME='SITES.DAT',TYPE='NEW')
OPEN(UNIT=15,NAME='MOMENT.DAT',TYPE='NEW')

C SPECIFY IVPAG PARAMETERS

NODES=12
TOL=0.9E-06
H=1.0E-10
PARAM(1)=H
MXSTEP=1000000000
PARAM(4)=MXSTEP
INORM=0
PARAM(10)=INORM
METH=2
PARAM(12)=METH
INDEX=1
TIDG=0.0

C READ DATA FILES AND PERFORM SUPPORTING ALGEBRAIC CALCULATIONS
CALL ALGBR

DO I=1,12
  Y(I)=DY(I)
ENDDO

C MAIN CALCULATION LOOP

T=0.0
ICOUNT=0
IFLAG=0
MEND=SINTIM*3600./TSTEP

RMWN=RMERMW*Y(5)/Y(4)
RMWW=RMERMW*Y(6)/Y(5)
RPD=RMWW/RMWN
WTETDY(3)*TETDMW*(VP/(VP+VW))*(100./1.077)*(1./.4)

10 FORMAT (7(1X,E9.4))

WRITE(13,10) T/3600.,RMWW,RMWN,RPD,Y(1)/TWO,Y(2),Y(3)/TTO
WRITE(14,10) T/3600.,Y(10),Y(11),Y(12),FS/FSO,FA/FAO,FV
WRITE(15,10) T/3600.,Y(4),Y(5),Y(6),Y(7),Y(8),Y(9)

DO M=1,MEND
  TIEND=TIDG+TSTEP
  T=TIEND

  C Adjust allylic chlorine rate constant

  IF (IFLAG.EQ.0.AND.(FA/FA0).LE.0.70) THEN
    RK3=RK3/5.0
    IFLAG=1
  ENDIF

  C Solve ODES

  CALL IVPAG(INDEX,NODES,FCN,FCNJ,A,TIDG, TIEND, 1
             TOL,PARAM,Y)
  ICOUNT=ICOUNT+1

C Calculate MW from moments and write results
IF(T.EQ.1.0.0R.ICOUNT.EQ.PCOUNT) THEN

FIRST=Y(5)+Y(8)
FETA=Y(5)/FIRST
FLAM=Y(8)/FIRST

RMWN=RMERMW*(FETA*Y(5)/Y(4)+FLAM*Y(8)/Y(7))
RMWW=RMERMW*(FETA*Y(6)/Y(5)+FLAM*Y(9)/Y(8))
RPD=RMWW/RMWN
WTETD=Y(3)*TETDMW*(VP/(VP+VW))*(100./1.077)*(1./.4)

WRITE(13,10) T/3600.,RMWW,RMWN,RPD,Y(1)/TWO,Y(2),Y(3)/TTO
WRITE(14,10) T/3600.,Y(10),Y(11),Y(12),FS/FSO,FA/FAO,FV
WRITE(15,10) T/3600.,Y(4),Y(5),Y(6),Y(7),Y(8),Y(9)
ICOUNT=0
ENDIF
ENDDO

C CLOSE DATA FILES
CLOSE(UNIT=13)
CLOSE(UNIT=14)
CLOSE(UNIT=15)
STOP
END

C********************************************************************************
C SUPPORTING ALGEBRAIC CALCULATIONS
SUBROUTINE ALGBR
DIMENSION DY(12)
COMMON/MISC/ ETA3,DY,PCOUNT,RMERMW,SIMTIM,TSTEP,TWO,TTO
COMMON/PART/ AP,RKM,RPC,SAP,SVP,VW
COMMON/RKS/ RK1,RK2,RK3,RK6,RK7,RKRED
COMMON/SITES/ FS,FA,FV,FSO,FAO,FV0
COMMON/STEP/ T,TETDMW,TEPMW,VP,STETD,STEPN
OPEN(UNIT=11,NAME='RCP1.DAT',TYPE='OLD')
OPEN(UNIT=12, NAME='CNST1.DAT', TYPE='OLD')

15 FORMAT(E10.4, 18( / E10.4))
20 FORMAT(E10.4, 22( / E10.4))

READ(11,15) GSUL,GTEPN,GTETD,STEPN,STETD,VW,WP,DPART,
1       DNM,FCONV,FSULINC,RMN,WM,FAO,FV0,TEMP,
1       TSTEP,SIMTIM,RPCOUNT
PCOUNT=RPCOUNT

READ(12,20) A1,ER1,A2,ER2,A3,ER3,A6,ER6,A7,ER7,
1       RMEDCOR1,RMEDCOR2,RMEDCOR3,RMEDCOR6,RMEDCOR7,
1       RKRED,RKM,RPC,RMONMW,SULMW,TEPMW,TEIDMW,RPI

C CALCULATE INITIAL CONDITIONS FOR ODEs

DY(1)=GTEPN*0.47/(TEPMW*VW) !TW
TW=2=DY(1)
DY(2)=0.0  !TP
VP=WP/DPART
DY(3)=GTETD/(TEIDMW*VP) !TT
TT=2=DY(3)

GSULINC=GSUL*FSULINC
RMERMW=RMONMW*(1.+GSULINC/(FCONV*100.))

DY(5)=FCONV*100./(RMONMW*VP) !ETA1
DY(4)=DY(5)/(RMN/RMERMW) !ETA0
DY(6)=DY(5)**(RMW/RMERMW) !ETA2
ETA3=(DY(6)/(DY(4)*DY(5)))*(2.*DY(4)*DY(6)—DY(5)**2.)

DY(7)=0.0  !ILAM0
DY(8)=0.0  !ILAM1
DY(9)=0.0  !ILAM2

C CALCULATE INITIAL SULFUR AND CHLORINE REACTIVE SITES

DY(10)=GSULINC/(SULMW*6.*VP) !RSO
DY(11)=FCONV*100.*FV0/(RMONMW*VP) !ACO
DY(12)=FCONV*100.*FV0/(RMONMW*VP) !VC0
FSO = DY(10)/DY(5)
FS = FSO
FA = FAO
FV = FVO

C CALCULATE RATE CONSTANTS

RK1 = A1*EXP(-ER1/TEMP) ! CC/MOL-SEC
RK2 = A2*EXP(-ER2/TEMP)
RK3 = A3*EXP(-ER3/TEMP)
RK6 = A6*EXP(-ER6/TEMP)
RK7 = A7*EXP(-ER7/TEMP)

C Apply medium correction

RK1 = RK1*RMEDCOR1
RK2 = RK2*RMEDCOR2
RK3 = RK3*RMEDCOR3*5.0
RK6 = RK6*RMEDCOR6
RK7 = RK7*RMEDCOR7

C CALCULATE MASS TRANSFER-RELATED VARIABLES

DCH = DN*1.0E-07
SAP = RPI*(DCH**2.)
SVP = (RPI/6.)*(DCH**3.)
RNP = VP/SVP
AP = SAP*RNP

CLOSE(UNIT=11)
CLOSE(UNIT=12)
RETURN
END

C**************************************************************************2
C DEB
SUBROUTINE FCN(NODES,TIDG,Y,YPRIME)
DIMENSION Y(NODES),YPRIME(NODES),DY(12)

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C Adjust k1 and k2 for sulfur linkage reactivity

RK1ADJ = RK1 * FS + 2. * RK1 * RKRED * (FS0 - FS)
RK2ADJ = RK2 * FS + 2. * RK2 * RKRED * (FS0 - FS)

YPRIME(1) = - (RKM * AP / VW) * (Y(1) - (1. / RPC) * Y(2))

IF (STEPN .GT. 0. AND. T .EQ. 86400.) THEN
  YPRIME(1) = YPRIME(1) + (GTEPN * 0.47 / (TEPMW * VW)) / TSTEP
ENDIF

YPRIME(2) = (RKM * SAP / SVP) * (Y(1) - (1. / RPC) * Y(2))
  1 - RK1ADJ * Y(2) * (Y(5) - Y(4)) + RK6 * Y(3) * Y(7)

YPRIME(3) = - RK6 * Y(3) * Y(7)

IF (STETD .GT. 0. AND. T .EQ. 86400.) THEN
  YPRIME(3) = YPRIME(3) + (STETD / (TETDMW * VP)) / TSTEP
ENDIF

ETA01 = 0.0
ETA02 = 0.0
ETA03 = 0.0
ETA06 = RK6 * Y(3) * Y(7)
ETA07 = 0.0
YPRIME(4) = ETA01 + ETA02 + ETA03 + ETA06 + ETA07

ETA11 = -(RK1ADJ * Y(2) / 2.) * (Y(6) - Y(5))
ETA12 = RK2ADJ * (Y(8) * (Y(5) - Y(4)) - (Y(7) / 2.) * (Y(6) - Y(5)))
ETA13 = RK3 * FA * Y(8) * Y(5)
ETA16 = RK6 * Y(3) * Y(8)
ETA17 = RK7 * FV * Y(8) * Y(5)
YPRIME(5) = ETA11 + ETA12 + ETA13 + ETA16 + ETA17

ETA21 = (RK1ADJ * Y(2) / 6.) * (Y(5) + 3.* Y(6) - 4.* ETA3)
ETA22 = RK2ADJ * (Y(9) * (Y(5) - Y(4)) + Y(8) * (Y(6) - Y(5)) -
1  \((Y(7)/6.)*(4.*\text{ETA3}-3.*Y(6)-Y(5))\)
\(\text{ETA23} = \text{RK3} \times \text{FA} \times (2.*Y(8) \times Y(6) + Y(9) \times Y(5))\)
\(\text{ETA26} = \text{RK6} \times Y(3) \times Y(9)\)
\(\text{ETA27} = \text{RK7} \times \text{FV} \times (2.*Y(8) \times Y(6) + Y(9) \times Y(5))\)
\(\text{YPRIME}(6) = \text{ETA21} + \text{ETA22} + \text{ETA23} + \text{ETA26} + \text{ETA27}\)
\(\text{ETA3} = (Y(6)/(Y(4) \times Y(5))) \times (2.*Y(4) \times Y(6) - Y(5)**2.)\)
\(\text{RLAM01} = \text{RK1ADJ} \times Y(2) \times (Y(5) - Y(4))\)
\(\text{RLAM02} = 0.0\)
\(\text{RLAM03} = -\text{RK3} \times \text{FA} \times Y(5) \times Y(7)\)
\(\text{RLAM06} = -\text{RK6} \times Y(3) \times Y(7)\)
\(\text{RLAM07} = -\text{RK7} \times \text{FV} \times Y(5) \times Y(7)\)
\(\text{YPRIME}(7) = \text{RLAM01} + \text{RLAM02} + \text{RLAM03} + \text{RLAM06} + \text{RLAM07}\)
\(\text{RLAM11} = (\text{RK1ADJ} \times Y(2)/2.) \times (Y(6) - Y(5))\)
\(\text{RLAM12} = -\text{RK2ADJ} \times (Y(8) \times (Y(5) - Y(4)) - (Y(7)/2.) \times (Y(6) - Y(5)))\)
\(\text{RLAM13} = -\text{RK3} \times \text{FA} \times Y(5) \times Y(8)\)
\(\text{RLAM16} = -\text{RK6} \times Y(3) \times Y(8)\)
\(\text{RLAM17} = -\text{RK7} \times \text{FV} \times Y(5) \times Y(8)\)
\(\text{YPRIME}(8) = \text{RLAM11} + \text{RLAM12} + \text{RLAM13} + \text{RLAM16} + \text{RLAM17}\)
\(\text{RLAM21} = (\text{RK1ADJ} \times Y(2)/6.) \times (Y(5) - 3.*Y(6) + 2.*\text{ETA3})\)
\(\text{RLAM22} = -\text{RK2ADJ} \times (Y(9) \times (Y(5) - Y(4)) - (Y(7)/6.) \times (2.*\text{ETA3} - 3.*Y(6) + Y(5)))\)
\(\text{RLAM23} = -\text{RK3} \times \text{FA} \times Y(5) \times Y(9)\)
\(\text{RLAM26} = -\text{RK6} \times Y(3) \times Y(9)\)
\(\text{RLAM27} = -\text{RK7} \times \text{FV} \times Y(5) \times Y(9)\)
\(\text{YPRIME}(9) = \text{RLAM21} + \text{RLAM22} + \text{RLAM23} + \text{RLAM26} + \text{RLAM27}\)
\(\text{YPRIME}(10) = -\text{RK1} \times \text{FS} \times Y(2) \times (Y(5) - Y(4))\)
\(\text{YPRIME}(11) = -\text{RK3} \times \text{FA} \times Y(5) \times Y(7)\)
\(\text{YPRIME}(12) = -\text{RK7} \times \text{FV} \times Y(5) \times Y(7)\)

\(\text{FS} = Y(10)/(Y(5) + Y(8))\)
\(\text{FA} = Y(11)/(Y(5) + Y(8))\)
\(\text{FV} = Y(12)/(Y(5) + Y(8))\)

\(\text{RETURN}\)
\(\text{END}\)

\(\text{SUBROUTINE FONJ(NODES,TIDG,Y,PD)}\)
DIMENSION Y(NODES), PD(NODES,NODES)
RETURN
END
C. Sample Input/Output File

**CNST1.DAT**

2.7500E+11 A1 frequency factor for \( k1 \) cc/mol sec
4.8660E+03 ER1 E/R for \( k1 \) K
4.6200E+11 A2 frequency factor for \( k2 \) cc/mol sec
4.5940E+03 ER2 E/R for \( k2 \) K
7.2200E+09 A3 frequency factor for \( k3 \) cc/mol sec
5.1690E+03 ER3 E/R for \( k3 \) K
3.7500E+11 A6 frequency factor for \( k6 \) cc/mol sec
4.6030E+03 ER6 E/R for \( k6 \) K
3.8800E+09 A7 frequency factor for \( k7 \) cc/mol sec
8.4980E+03 ER7 E/R for \( k7 \) K
4.0000E-02 RMEDCOR1 medium corr for \( k1 \)
3.0000E-03 RMEDCOR2 medium corr for \( k2 \)
3.1500E-02 RMEDCOR3 medium corr for \( k3 \)
2.5000E-03 RMEDCOR6 medium corr for \( k6 \)
3.1500E-02 RMEDCOR7 medium corr for \( k7 \)
1.0000E-02 RKRED reactive site access corr
6.4000E-10 RKM mass transfer coeff cm/sec
6.6667E-03 RPC Tepidone partition coeff
8.8540E+01 RMONMW monomer MW g/mole
3.2060E+01 SULMW sulfur MW g/mole
2.2739E+02 TEPMW Tepidone MW g/mole
2.9656E+02 TETD MW g/mole
3.1416E+00 pi
RCP1.DAT

0.6000E+00 GSUL grams S phm
0.7990E+00 GTEPN grams Tepidone N phm
0.4348E+00 GTETD grams TETD phm
0.0000E+00 STEPN grams step Tepidone N phm
0.0000E+00 STETD grams step TETD phm
1.1533E+02 VW aqueos volume cc phm
1.0663E+02 WP particle phase g phm
1.1603E+00 DPART particle phase g/cc
1.0000E+02 DNM wgt-avg particle diam nm
0.8400E+00 FCONV frac conv at begin pep
0.5000E+00 FSULINC frac recipe S incor in polymer
1.0500E+05 RMN MWn of unpeptized polymer g/mole
1.5790E+06 RMW MWw of unpeptized polymer g/mole
0.0100E+00 FAO init frac allylic Cl
0.9900E+00 FVO init frac vinyl Cl
3.1315E+02 TEMP temperature K
1.0000E+01 TSTEP ODE solution freq sec
2.0000E+01 SIMTIM simulation time hrs
3.6000E+01 PCOUNT data write count
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continued . . .

continued . . .

continued . . .

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APPENDIX IV

Indexing Terms

G-TYPE NEOPRENE
AGING
PEPTIZATION
MATHEMATICAL MODEL