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Characterization and Selection of Hydroxyl-Terminated Polybutadiene Polymers for High-Strain Applications

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The University of Southern Mississippi

Characterization and Selection of Hydroxyl-Terminated Polybutadiene Polymers for
High-Strain Applications

by

Nathaniel Prine

A Thesis
Submitted to the Honors College of
The University of Southern Mississippi
in Partial Fulfillment
of the Requirements for the Degree of
Bachelor of Science
in the Department of Polymer Science

May 2018

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Abstract

Understanding the behavior of hydroxyl-terminated polybutadiene (HTPB) as a composite matrix is imperative for the development of future military and aerospace munition technology. As a vital component of solid rocket fuel, HTPB strongly contributes to the fatigue behavior, burn-rate, and other properties that can cause critical failure of the rocket if not formulated properly. The purpose of this research is to identify traits characteristic of poor-performing HTPB matrices by analyzing two samples labeled as either “good” or “bad” based on their performance as a fuel matrix. Samples were analyzed *via* ^1H NMR and GPC to determine their epoxy content, hydroxyl distribution, and molecular weight. Results revealed marginal differences in all three categories, with the sample labeled “bad” possessing higher epoxy content, higher molecular weight, and a higher hydroxyl equivalent weight. Conclusively, further study is required to definitively claim these factors actively contribute to the poor performance of HTPB, however it was confirmed there are key differences in both morphology and molecular weight between the two samples analyzed.

Dedication

To my sister Katie:

Thank you for your unending patience and
always laughing at my bad jokes.

Acknowledgements

I would like to thank my thesis advisor, Dr. Robson Storey, for mentoring me through my entire undergraduate career and allowing me to actively participate in research. Additionally, I am entirely indebted to Dr. Heather Broadhead for her tireless contributions to my undergraduate education and always keeping my best interests at heart. As my previous graduate mentor, I would like to thank Hunter Cooke for always holding me accountable and teaching me how to gain wisdom from the failures and successes of others. Lastly, I could not have made it to this point in my career without the unending encouragement and support of my family who put up with my sleepless study nights and long scientific rants.

Table of Contents

List of Tables.....	viii
List of Figures.....	ix
List of Abbreviations.....	x
Chapter 1: Introduction.....	1
Chapter 2: Literature Review of HTPB Propellant	3
Structural Characteristics of HTPB.....	3
Oxidation Formations in HTPB.....	6
Review of Potential Methods for Determining Hydroxyl Content.....	8
Chapter 3: Methodology.....	8
Nuclear Magnetic Resonance Analysis.....	9
Determination of Epoxide Content.....	9
Determination of Cis/Trans/Vinyl Content.....	10
Hydroxyl Distribution by Nuclear Magnetic Resonance (NMR).....	10
Molecular Weight by Gel Permeation Chromatography (GPC).....	11
Chapter 4: Results and Discussion.....	12
Chapter 5: Conclusion.....	18
Direction on Future Research.....	18
References.....	19

List of Tables

Table 1: Epoxide Content of R45M HTPB.....	14
Table 2: Cis/Trans/Vinyl Content of HTPB Samples.....	14
Table 3: Hydroxyl Equivalent Weight of HTPB Samples.....	15
Table 4: Hydroxyl Composition of HTPB Samples.....	15
Table 5: Molecular Weight Analysis of HTPB Samples.....	16
Table 6: Predicted Intrinsic Viscosity of HTPB Samples.....	17

List of Figures

Figure 1: Free Radical Polymerization of HTPB.....	3
Figure 2: Formation of V-type and H-type Hydroxyls.....	4
Figure 3: Formation of G-type Hydroxyls.....	4
Figure 4: Proton NMR Spectra of HTPB.....	5
Figure 5: Carbon NMR Spectra of HTPB.....	5
Figure 6: Post-Synthesis Formation of Secondary Hydroxyls in the HTPB Backbone.....	6
Figure 7: Formation of Epoxides Along the HTPB Backbone.....	7
Figure 8: Strain Characteristics of Cured HTPB Matrices.....	8
Figure 9: NMR Spectra of "Bad" HTPB Sample.....	12
Figure 10: NMR Spectra of "Good" HTPB Sample.....	12
Figure 11: Hydroxyl and Epoxide Peaks of "Bad" HTPB.....	13
Figure 12: Hydroxyl and Epoxide Peaks of "Bad" HTPB.....	13

List of Abbreviations

AMRDEC	Aviation and Missile Research Development and Engineering Center
CDCl ₃	Deuterated Chloroform
DRI	Differential Refractive Index
GPC	Gel Permeation Chromatography
HTPB	Hydroxyl-Terminated Polybutadiene
MALDI	Matrix Assisted Laser Desorption Ionization
MALS	Multi-Angle static Light Scattering
NMR	Nuclear Magnetic Resonance
NOE	Nuclear Overhauser Effect
TMS	Tetramethylsilane
TOF-MS	Time of Flight-Mass Spectrometry

Chapter 1: Introduction

Hydroxyl-terminated polybutadiene (HTPB) is utilized heavily as a polymer matrix in solid rocket propellants and cast-cure explosives. Given its significant role in tactical ordnance, there is an urgent need to develop reliable test methods for determining suitable grades of HTPB polymers for high-strain propellant formulations. The purpose of this methodology development is to distinguish between acceptable and problematic grades of HTPB. Research by the U.S. Aviation and Missile Research Development and Engineering Center (AMRDEC) and The University of Southern Mississippi showed that cured propellant mixes undergo stress-cracking, creating additional sites of combustion within the missile casing and risking failure of the rocket module.¹ Additionally, reducing the risk of rocket failure is highly dependent upon both the synthesis and processing methodology used by manufacturers of HTPB. Persistent oxidation of the unsaturated moiety by residual peroxide initiator leads to the formation of epoxides, possibly causing polymer embrittlement.² To combat the aforementioned potential risk of motor failure, this study statistically characterizes HTPB samples via Gel Permeation Chromatography (GPC) and Nuclear Magnetic Resonance Spectroscopy (NMR) to define key structural differences between suitable and problematic grades of HTPB with the intention of providing greater insight into the development of reliable polymer matrices for the formulation of solid rocket fuel. We hypothesize the variation of strain capacity in suitable and problematic grades of HTPB is directly related to differences in molecular weight, polydispersity index, epoxide content, olefin stereochemistry, and mid-chain hydroxyl content.

There are four significant leads that may distinguish between the suitable and problematic grades of HTPB. The first is the existence of mid-chain, geraniol (G-type)

alcohol groups within the polymer structure.³ It is suspected that the G-type alcohols may contribute to the accelerated formation of epoxides and affect the strain capabilities of the polymer. However, the existence of G-type moieties within the structure of HTPB is controversial within the literature due to contradicting proton assignments in NMR spectroscopy. The epoxide content of HTPB is the second known indicator of low strain capabilities. Research by Haas suggests HTPB containing less than 3% combined cis and trans epoxy groups yields higher strain capacity.² The third area of investigation was the statistical distribution of hydroxyl moieties stemming from the backbone of the polymer chain. By the addition of a diisocyanate curator, samples containing a higher hydroxyl functionality will form higher density crosslinking than samples with a lower functionality. The fourth investigation was of the cis and trans H-type hydroxyls within problematic and suitable grades of HTPB. Haas demonstrates a strong correlation between higher cis hydroxyl content and lower strain capacities.

Proposed methods for the quantitative analysis of hydroxyl content, epoxide content, and molecular weight included proton nuclear magnetic resonance spectroscopy and gel permeation chromatography. The result of this research revealed characteristic trends within HTPB samples, allowing formulators to distinguish suitable grades of HTPB for both exploratory and tactical applications.

Chapter II: Literature Review of HTPB Propellant

Structural Characteristics of HTPB

Chemical manufacturers synthesize hydroxyl-terminated polybutadiene via free radical polymerization in the presence of an alcohol solvent. The process involves the radical initiation of 1,3-butadiene using hydrogen peroxide. Propagation occurs to form a combination of cis, trans, and vinyl alkenes along the backbone of the polymer chain.⁴ Termination then occurs primarily by combination of two macroradicals.

(Figure 1).

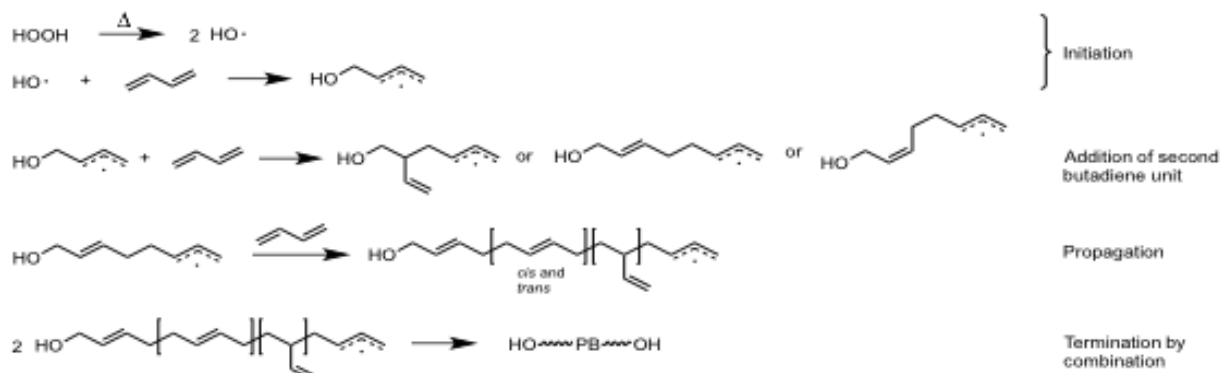


Figure 1. Free Radical Polymerization of HTPB⁴

Three main types of hydroxyl functionalities formed during synthesis are V-type, H-type, and G-type hydroxyls.⁴ V-type and H-type hydroxyls are formed during initiation, when a primary hydroxyl radical adds to a 1,3-butadiene monomer (Figure 2). The resulting resonance stabilized radical can be attacked by a second butadiene monomer either at C2 or C4. The former attack results in a V-type hydroxyl; the latter attack results in an H-type hydroxyl, either cis or trans. The third type of functionality is the G-type hydroxyl formed

by chain transfer caused by the abstraction of a hydrogen from the tertiary carbon located in the 1,2-vinyl structural unit (Figure 3).

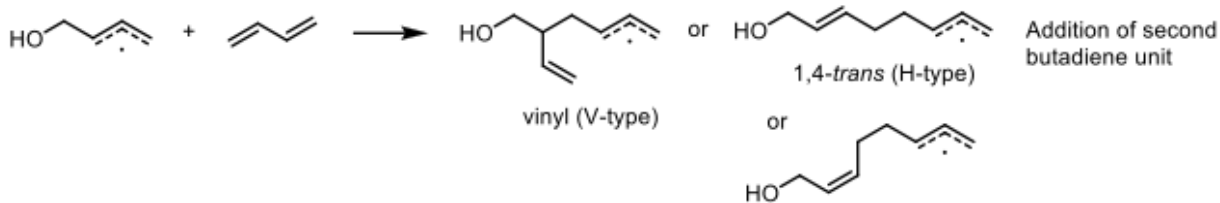


Figure 2. Formation of V-type and H-type Hydroxyls⁴

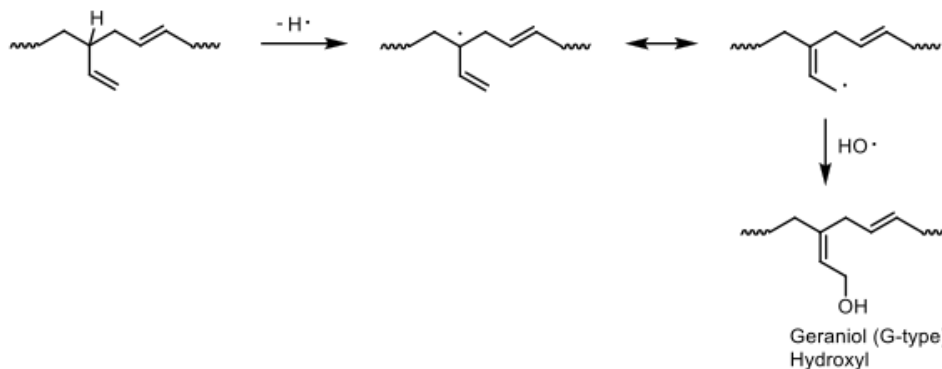


Figure 3. Formation of G-type Hydroxyl⁴

The G-type hydroxyl is perhaps the most controversial of the three documented formations due to the challenges in differentiating the methylene protons adjacent to the G-type hydroxyl from the methylene protons found in the H-type hydroxyl in proton NMR spectra. The peak assignments in Figure 4 were originally proposed by Fages and Pham.⁵ However, Mahanta and Pathak assign the peak at 4.2 ppm to cis-1,4 hydroxyl end groups and the peak at 4.1 ppm to trans-1,4 hydroxyl end groups.^{4,6} Fages and Pham also provide assignments for the carbon NMR spectra of HTPB.⁵ Figure 5 indicates the locations of the

three hydroxyl functionalities at 63.5 ppm (H-type), 65.0 ppm (V-type), and 58.2 ppm (G-type) as provided by Cooke, et al.⁴

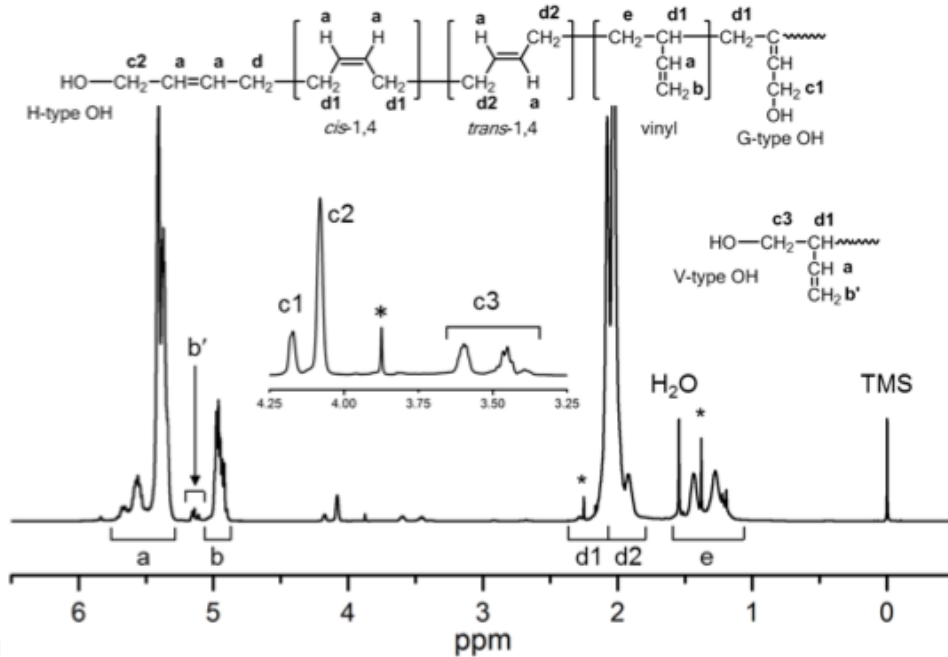


Figure 4. Proton NMR Spectra of HTPB⁴

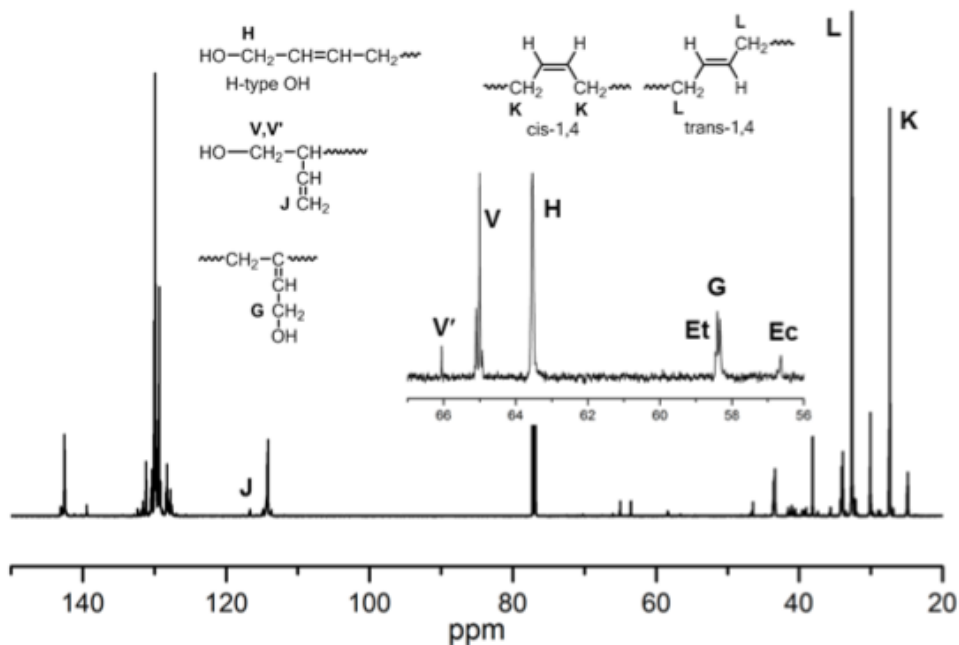


Figure 5. Carbon NMR Spectra of HTPB⁴

Oxidation Formations in HTPB

The hydroxyl content of HTPB is an important factor in propellant formulations and is generally dependent upon the initial initiator concentration during synthesis. In a study by Cooke III, et al., the molecular weight, polydispersity, structural characteristics, and hydroxyl content of 24 different thermally-aged samples of HTPB were analyzed.⁴ The study revealed a correlation between molecular weight, hydroxyl content, and sample age. As the samples aged, the hydroxyl equivalent weight decreased and the molecular weight increased, indicating an increase in hydroxyl content.⁴ As previously stated, the hydroxyl content depends strongly on the initiator concentration added during synthesis. Because of the increase in hydroxyl content with no apparent external source of oxidation, it is probable there remains residual peroxide initiator in commercially-synthesized HTPB.⁴ These hydroxyls formed post-synthesis are not considered to be G-, H-, or V-type because of their unique secondary position with respect to the carbon backbone (Figure 6). However, these secondary hydroxyl functionalities are not acknowledged in the literature and theoretically could be prevented simply by utilizing a radical trap to absorb residual initiator.

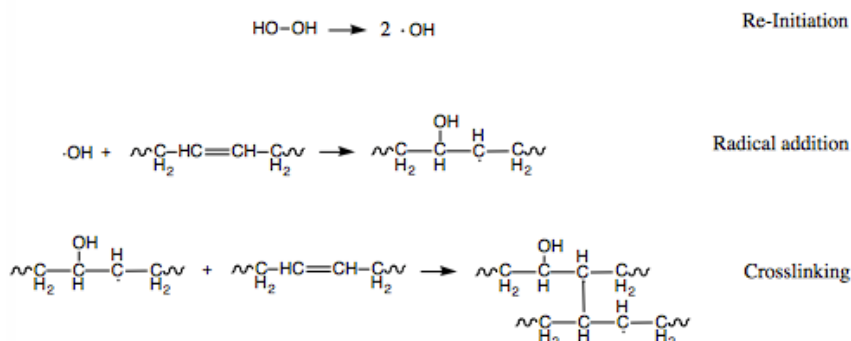


Figure 6. Post-Synthesis Formation of Secondary Hydroxyls in the HTPB Backbone

In contrast to the formation of secondary hydroxyls, the formation of epoxides within the structure of HTPB is a well-documented occurrence. The formation of epoxides along the unsaturated backbone is a concerted mechanism which involves oxidation at the points of unsaturation by inactive peroxides such as a peracid which are also known initiators for the synthesis of HTPB (Figure 7).⁵ The significant role epoxides play in the mechanical properties of HTPB is well documented in literature. Research by Haas reveals that higher epoxide content within HTPB can impart significantly lower strain capacity to crosslinked matrices than samples containing negligible epoxide content.⁷

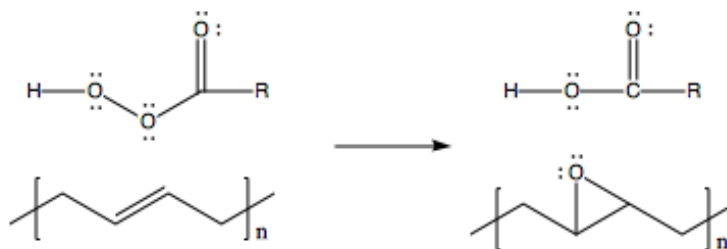


Figure 7. Formation of Epoxides Along the HTPB Backbone

Along with epoxides, Haas also discusses the role V-type hydroxyls play in the strain capacity of HTPB. In patent 4,536,236, Haas neutralizes the effect of the epoxides on the properties of HTPB by reacting the epoxide functionalities with a monofunctional isocyanate.⁷ The terminal V-type hydroxyls are separated into classes of either cis-hydroxyl or trans-hydroxyl. Samples containing high and low concentrations of cis-hydroxyl were cured by the addition of an isocyanate curator. The Young's modulus of each sample was tested and the results show samples containing a higher concentration of cis-hydroxyl possessed a lower strain capacity (Figure 8).⁷

Sample	Cis Hydroxy ^a	Curative ^b	Approximate Strain (%) ^c
A	15	DDI	570
B	15	DDI	480
C	15	HMDI	330
D	15	HMDI	280
E	18	HMDI	190
F	19	DDI	270
G	20	DDI	180
H	23	DDI	180

^aBy ¹³C NMR analysis, includes contribution of epoxy.

^bDDI stands for dimeryldiisocyanate; HMDI stands for hexaxethylenediisocyanate.

^cASTM procedure.

Figure 8. Strain Characteristics of Cured HTPB Matrices⁷

Review of Potential Methods for Determining Hydroxyl Content

Titrimetry and NMR analysis are the most common methods for detection of relative hydroxyl content. The titrimetric method involves the use of an excess of a strong acid to acetylate the hydroxyls and then back-titrating samples to a pre-determined pH.⁴ A blank sample is required, which contains all reagents, with the exception of HTPB. The volumetric difference in base added is then used to calculate hydroxyl equivalent weight and hydroxyl content. This method is both time-consuming and heavily reliant upon environmentally harmful solvent. The environmentally friendly alternative to analytical titrimetry is NMR analysis. The main obstacle for smaller laboratories adopting the NMR method is instrument cost. However, if obtained, NMR can be an effective tool for evaluating hydroxyl content.

Chapter III: Characterization Methodology

The focus of this methodology was to analyze two grades of HTPB. Manufacturers have labeled grade A as suitable and grade B as problematic by physical testing procedures. The two grades of HTPB were sourced from an undisclosed entity. By utilizing the

following nondestructive methods, the differences in structure, hydroxyl content, molecular weight, and epoxide content of the two grades were established.

Nuclear Magnetic Resonance (NMR) Analysis

NMR analysis of the two HTPB samples followed the procedure given by Cooke, et al.⁴ Quantitative ¹H spectral data of the two grades of HTPB was obtained using a Bruker® Ascend (TopSpin 3.5) NMR spectrometer operating at a frequency of 600.13 MHz and equipped with a standard 5 mm two channel probe.⁴ A t1 experiment for HTPB was completed and the longest relaxation time was determined for sample concentrations of 2.5% (w/v) in CDCl₃.⁴ Sample solutions were contained and analyzed within 5 mm NMR tubes. A total of 32 scans were acquired per sample and the shifts were automatically referenced by the TopSpin 3.5 software using the resonance frequency of TMS in CDCl₃ at 0 ppm.⁴

Determination of Epoxide Content

For the detection of epoxide functionalities within the polymer chain, a 30 weight % solution of HTPB in CDCl₃ was charged to a 5 mm NMR tube and shaken to ensure a homogenous mixture. A ¹H NMR spectrum was obtained. To suppress the NOE, composite pulse decoupling during data acquisition was utilized. A total of 32 scans was obtained, as implemented by Holbrook, et al.⁸ Parameters such as acquisition time and pre-scan delay were selected upon the completion of a t1 experiment for the given concentration. Data acquisition took place at a temperature of 303.1 K. Once the integrations corresponding to each peak were determined, equation 1 was used to quantify the total epoxide content of the sample.

$$f_{\text{epoxide,1H}} = \frac{2(A_{c4} + A_{c5})}{\left(\frac{3A_b}{2} + A_{c1} + A_{c2} + A_d\right)} \quad 1)$$

Determination of Cis/Trans/Vinyl Content

The cis-1,4, trans-1,4, and 1,2-vinyl content of the two grades of HTPB was determined via ^1H NMR. According to Holbrook, et al., the acquisition time for obtaining ^1H is significantly less than obtaining a ^{13}C spectrum to distinguish the stereochemistry of the 1,4 moieties.⁸ The fraction of vinyl repeat units (f_{vinyl}) will be calculated using equation 2, where A_b , A_b , and $A_{b'}$ signify the area of integration for the V-type, 1,2-vinyl additions, and 1,4-vinyl olefinic regions indicated in figure 4.⁸

$$f_{\text{vinyl}} = \frac{2(A_b + A_{b'})}{2A_a + (A_b + A_{b'})} \quad 2)$$

Once the vinyl content was obtained, the fraction of cis-1,4 ($f_{\text{cis-1,4}}$) and trans-1,4 ($f_{\text{trans-1,4}}$) was then calculated using the equation 3 and 4 where ‘A’ values signify the areas of integration for the cis-1,4 and trans-1,4 moieties.

$$f_{\text{cis-1,4}} = \frac{(2A_{d1} - A_b)(2A_a - A_b)}{(2A_{d1} - A_b + 2A_{d2})(2A_a + A_b)} \quad (3)$$

$$f_{\text{trans-1,4}} = \frac{2A_{d2}(2A_a - A_b)}{(2A_{d1} - A_b + 2A_{d2})(2A_a + A_b)} \quad (4)$$

Hydroxyl Distribution by Nuclear Magnetic Resonance (NMR)

Previously acquired quantitative ^1H spectra were analyzed and the hydroxyl content of each sample was determined by integrating the peaks corresponding to the V-type, H-type, and G-type hydroxyls. Deconvolution of the G-type peak was required and completed using MestreNova software. Equations 5 and 6 were utilized to solve for the hydroxyl content, hydroxyl equivalent weight, and hydroxyl composition, where N_{OH} is the number

of moles of hydroxyl groups, FW_{BD} is the formula weight of butadiene (54.01 Da), and FW_{OH} is the formula weight of a hydroxyl group (17.01 Da).

$$N_{OH} = \frac{A_{c1}}{2} + \frac{A_{c2}}{2} + \frac{A_{c3}}{2} \quad 5)$$

$$OH \text{ eq wt} = \left(\frac{3A_b}{4} + \frac{A_{c1} + A_{c2} + A_d}{2} \right) \frac{FW_{BD}}{A_c} + FW_{OH} \quad 6)$$

The fraction of V-type, H-type, and G-type was determined by dividing the peak area of each functionality by the sum of the total hydroxyl integrations.

Molecular Weight by Gel Permeation Chromatography (GPC)

A concentration of 0.01 g of polymer per 1.5 g THF was charged to a 20 mL scintillation vial using a 1 mL syringe and a glass pipette. A 1 mL syringe was used to extract the solution and a 25 mm syringe filter attached before adding the mixture to a GPC vial. A Waters® 2695 Separations Module equipped with a Wyatt Optilab® T-rEX differential Refractive Index (DRI) detector and a Wyatt miniDAWN® TREOS® Multi-Angle static Light Scattering (MALS) detector. Experiments were operated from the Wyatt Astra® software and Waters Empower® software. This procedure allowed the differences in absolute molar mass, concentration, and polydispersity index of the HTPB samples to be determined.

Chapter IV: Results and Discussion

Nuclear Magnetic Resonance Analysis

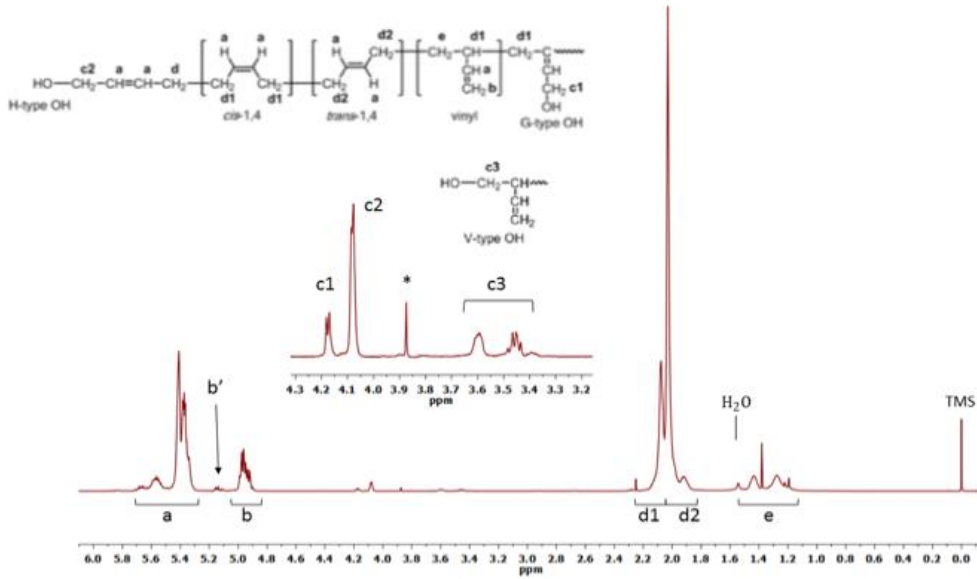


Figure 9. NMR Spectra of "Bad" HTPB Sample

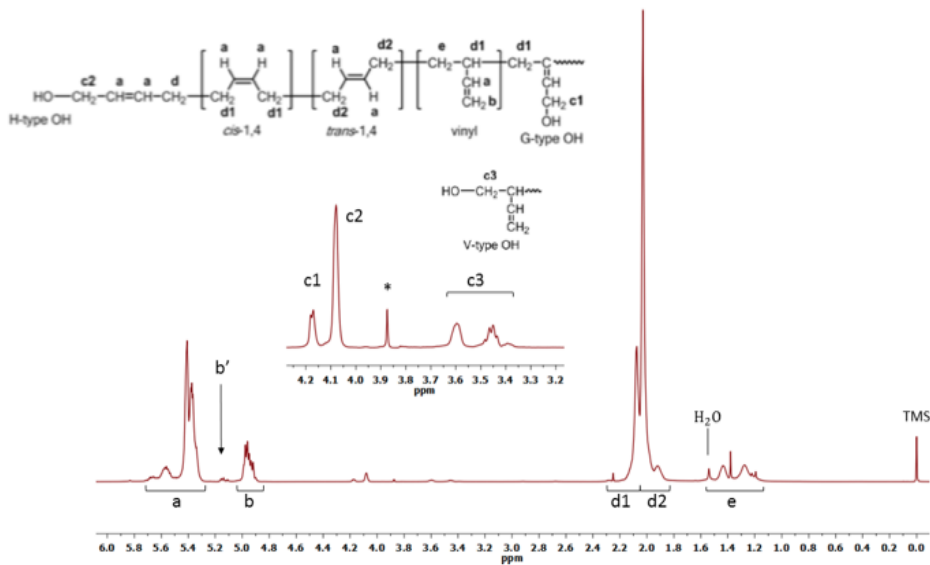


Figure 10. NMR Spectra of "Good" HTPB Sample

Epoxide Content by NMR Analysis

HTPB samples pre-labeled “good” and “bad” by the supplier based on their performance were examined to determine their epoxide content. By integrating the peaks corresponding to the epoxidized repeat units, the epoxide content of each sample was determined.

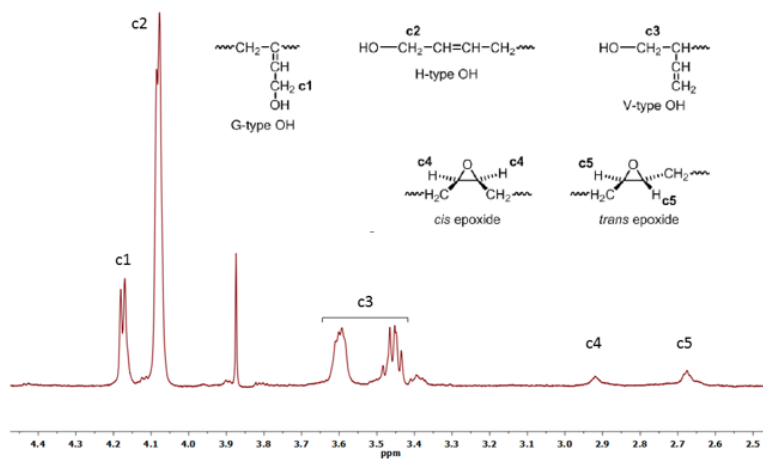


Figure 11. Hydroxyl and Epoxide Peaks of "Bad" HTPB

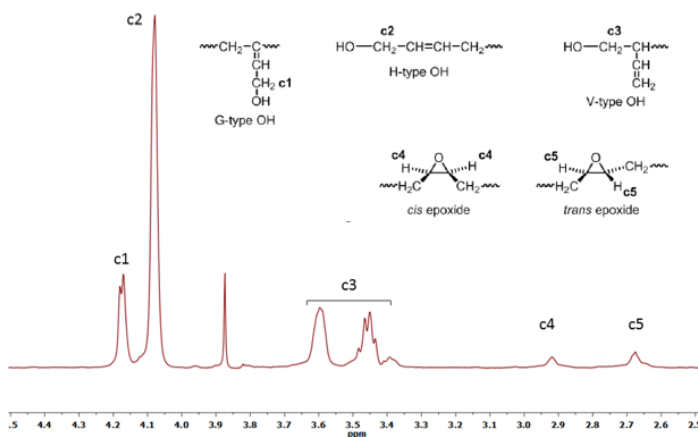


Figure 12. Hydroxyl and Epoxide Peaks of "Good" HTPB

Table 1. Epoxide Content of R45M HTPB.

Sample	Epoxide Content (%)
R45M “Bad”	0.241
R45M “Good”	0.235

Analysis revealed the epoxide content of the bad sample was marginally higher than that of the good sample. While seemingly insignificant, the higher epoxide functionality may contribute to the poor performance of the bad HTPB matrix. Poor performance may be associated with the brittleness of the matrix, which directly correlates to greater crosslink density. As the number of epoxide moieties increases, the probability of intramolecular and intermolecular reactions with terminal and mid-chain hydroxyls also increases. Understanding the poor thermal stability of epoxies in relation to their di-substituted alkene precursors, higher epoxide functionalities in HTPB matrices may serve as an indicator of poor matrix performance.

Cis/Trans/Vinyl Content by NMR Analysis

Table 2. Cis/Trans/Vinyl Content of HTPB Samples.

Sample	f(1,4-Cis) %	F(1,4-Trans) %	f(Vinyl) %
R45M “Bad” HTPB	23.7	55.6	20.7
R45M “Good” HTPB	25.4	54.2	20.4

The distribution of unsaturated moieties within both samples of HTPB was found to be quite similar with only a slight difference in isomeric content. The “bad” sample contained a higher percentage of 1,4-trans isomers than did the “good” sample, however this does not seem to correlate well to poor matrix performance in terms of stability. Traditionally, the trans isomer is cited as the more stable of the two substitution configurations as its heat of hydrogenation is approximately 4 kJ/mol less than that of its

cis counterpart.⁹ Following this line of logic, it would appear the sample containing higher trans isomeric content would prove the most stable of the two. However, in this case, the “bad” HTPB sample, which is cited as the least stable by the distributor, appears to contain a greater trans isomeric content than the “good” sample. The relatively higher vinyl content of the “bad” sample suggests a stronger link to poor performance as vinyl branching may reduce the ability of the polymer chains to form short-range regions of crystallinity. While not quantified, the transparent qualities of both samples indicate a highly amorphous material. By reducing the ability of the polymer chains to form ordered regions, the overall stability of the system may also be reduced. While further experimentation is required to validate this hypothesis, a higher percentage of trans content may correlate to poor matrix performance.

Hydroxyl Content by NMR Analysis

Table 3. Hydroxyl Equivalent Weight of HTPB Samples.

Sample	OH Eq. Weight (Da)
R45M “Bad” HTPB	1572.13
R45M “Good” HTPB	1520.75

Table 4. Hydroxyl Composition of HTPB Samples.

Sample	f(G-type) %	f(H-type) %	f(V-type) %
R45M “Bad” HTPB	14	53	33
R45M “Good” HTPB	15	52	33

NMR analysis revealed the hydroxyl equivalent weight was marginally higher in the “bad” HTPB sample than the “good” sample. As the hydroxyl equivalent weight describes the number of grams of a substance per hydroxyl functionality, the higher hydroxyl functionality of the “good” sample may contribute to its higher stability. Through hydrogen bond interactions among polymer chains, the cohesion between polymer strands

is increased and reduces the overall probability of material fracture. Additionally, there did not appear to be a strong difference between samples in regard to hydroxyl composition because the percentage of V-type hydroxyls was found to be equivalent in both “good” and “bad” matrices. There was a slight variance in G-type and H-type composition; the “good” sample contained a higher percentage of G-type hydroxyls. While the previous hypothesis held that a higher number of mid-chain hydroxyl functionalities contributes to lower matrix performance, it does not appear to hold true in this case. In contrast to this idea, the added mid-chain functionality may actually improve the cohesion between polymer strands through increased hydrogen bonding activity. However, further experimentation using rheometry is required to validate this hypothesis.

Molecular Weight Determination by GPC

Table 5. Molecular Weight Analysis of HTPB Samples.

Sample	$M_n \times 10^3$ (Da)	$M_w \times 10^3$ (Da)	PDI
R45M Good A	4.399	6.760	1.537
R45M Good B	3.918	6.080	1.552
R45M Bad A	6.021	8.932	1.483
R45M Bad B	5.829	8.857	1.520
	Avg.	Avg.	Avg.
R45M Good	4.159	6.420	1.544
R45M Bad	5.925	8.895	1.501

Analysis by gel permeation chromatography revealed the strongest contrast between the two samples, with their number-average and weight-average molecular weights varying by up to 2,000 Da. As shown in table 5, while both samples displayed similar polydispersity, the “bad” sample possessed a significantly higher molecular weight relative to the “good” sample. The exact reason for higher molecular weight corresponding to lower matrix performance is unclear, however one possible explanation lies in the

dispersion of hydroxyls along the polymer backbone. A linear polymer strand of higher molecular weight would have a higher number of hydroxyls per chain and would demonstrate a higher number of intramolecular interactions than intermolecular interactions with neighboring chains as longer polymer chains tend to exist in the coiled state according to Gaussian statistical theory.¹⁰ The more coiled a polymer chain becomes, the higher the probability of intramolecular interaction.

Relationship between Molecular Weight and Viscosity

In addition, there is a strong correlation between molecular weight and matrix viscosity that becomes critical in solid fuel formulation. Higher matrix viscosity may prevent the uniform mixing of additional fuel components, such as ammonium perchlorate nanoparticles, and thereby create non-uniform combustion of the composite fuel. As a hypothetical calculation and taking the viscosity-average molecular weight to be the average of the number-average and weight-average molecular weight, the Mark-Houwink equation (equation 7) may be used to estimate the intrinsic viscosity of the two samples,

$$[\eta] = KM^\alpha \tag{7}$$

where $[\eta]$ is intrinsic viscosity, M is viscosity-average molecular weight, and K and α are constants specific to the 1,4-polybutadiene in THF polymer/solvent system as provided by the American Polymer Standards Corporation.¹¹ Using these parameters, the following values may be estimated (table 6):

Table 6. Predicted Intrinsic Viscosity of HTPB Samples

Sample	α/K (dL/g)	$M \times 10^3$ (Da)	$[\eta]$ (dL/g)
R45M “Bad” HTPB	0.44/0.0076	7.41	0.383
R45M “Good” HTPB	0.44/0.0076	5.29	0.330

While this calculation does not take into consideration the effect of the hydroxyl end groups and mid-chain functionalities, it serves as a qualitative estimate of how the polymer contributes to the overall viscosity of the polymer/solvent system. From this data, the intrinsic viscosity appears slightly higher in the “bad” sample as compared to the “good” sample. While the difference appears insignificant, this small difference in intrinsic viscosity may indirectly contribute to the poor performance of HTPB matrices.

Chapter V: Conclusion

The gathered data represent quantitative measurements of the epoxide content, cis/trans/vinyl isomeric content, hydroxyl content, and molecular weight values as well as qualitative estimates of the intrinsic viscosity of HTPB samples labeled as “good” and “bad” on the basis of performance. The purpose of this study was to define traits that characterize HTPB samples on the basis of performance. While this study is by no means exhaustive, the characterization methods utilized were able to detect definitive differences between the two samples in all measured and estimated values. Conclusively, qualities corresponding to the poor performing HTPB sample include higher epoxide concentration, vinyl content, hydroxyl equivalent weight, molecular weight, and lower G-type hydroxyl content.

Direction on Future Research

Future work is needed on this topic to develop a clearer understanding of HTPB as a polymer matrix. Samples should be further analyzed in whole-batch studies in terms of

viscosity, molecular weight, and morphology to accurately distinguish suitable grades of HTPB and advance solid-rocket fuel technology.

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