THE SYNTHESIS AND CHARACTERIZATION OF ENERGETIC MATERIALS FROM SODIUM AZIDE

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THE SYNTHESIS AND CHARACTERIZATION OF
ENERGETIC MATERIALS FROM SODIUM AZIDE

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This thesis is dedicated to M. G.

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LIST OF ABBREVIATIONS

BHT — 5,5'-bi-1*H*-tetrazole

BTEACH — benzyltriethylammonium chloride

DMAZ — dimethylethylamino azide

DMSO — dimethylsulfoxide

DSC — differential scanning calorimetry

ECH — epichlorohydrin

GAP — glycidyl azide polymer

GPC — gel permeation chromatography

GTP — glycidyl tetrazole polymer

IR — infrared spectroscopy

Isp — specific impulse

MMH — monomethylhydrazine

5-MT — 5-methyltetrazole

NaEDTA — sodium ethylenediaminetetraacetic acid

NMR — nuclear magnetic resonance

O/F — oxidizer/fuel ratio

PDI — polydispersity index

PECH — polyepichlorohydrin

5-PT — 5-phenyl-1*H*-tetrazole

PTC — phase transfer catalysis

TBAB — tetrabutylammonium bromide

TEAHC triethylamine hydrochloride

TFA trifluoroacetic acid

SUMMARY

A tetrazole is a 5-membered ring containing 4 nitrogens and 1 carbon. Due to its energetic potential and structural similarity to carboxylic acids, this ring system has a wide number of applications. In this thesis, a new and safe sustainable process to produce tetrazoles was designed that acheived high yields under mild conditions. Also, a technique was developed to form a trityl-protected tetrazole *in situ*. The rest of this work involved the exploitation of the energetic potential of tetrazoles. This moiety was successfully applied in polymers, ionic liquids, foams, and gels. The overall results from these experiments illustrate the fact that tetrazoles have the potential to serve as a stable alternative to the troublesome azido group common in many energetic materials. Due to these applications, the tetrazole moiety is a very important entity.

CHAPTER I

INTRODUCTION

A tetrazole is a 5-membered ring containing 4 nitrogens and 1 carbon. Due to its energetic potential and structural similarity to carboxylic acids, this ring system has a wide number of applications. Tetrazoles are used in the pharmaceutical industry in modern anti-hypertensive medications. While this field is fairly developed, the energetic applications for tetrazoles are fairly unexplored. Throughout this thesis, tetrazole derivatives were synthesized and investigated as potential energetic materials or components of energetic materials. In most cases, these compounds were an acceptable substitute for the problematic azido derivatives common in many energetic compounds. Specifically, azido groups are unstable because they react with a variety of compounds. In energetic binders, they react with the cure catalysts and introduce charges along the polymer chains. These problems will be further defined and discussed in the following chapters.

The synthesis of tetrazoles is inherently dangerous because of the explosive and toxic nature of sodium azide. One of the initial goals of this research was to design a safe and efficient synthesis of tetrazoles. In Chapter II, two novel systems that used benzonitrile as reactant and solvent for the preparation of 5-phenyl-1H-tetrazole were developed. The first reaction system used a protonated tertiary amine (a proton source) and sodium azide. This reaction was run at a relatively mild temperature of 50 $^{\circ}$C to provide an isolated product yield of 97% within 16 hours. This versatile reaction system also produced a protected tetrazole *in situ* with the addition of trityl chloride in place of the usual acidification step. The second reaction system, employing quaternary

ammonium salts, demonstrated the ability to control the potential amount of hydrazoic acid formation while producing good yields of 5-phenyl-1H-tetrazole in relatively mild conditions. By introducing only a 10 mol% of a proton source in the presence of a stoichiometric amount of quaternary ammonium salt, isolated yields as high as 87 % were achieved.

In Chapters III and IV, the synthesis of energetic polymers that included tetrazole derivatives as sidechains on the polymer backbone was achieved. These polymers were designed as an improvement upon glycidyl azide polymers described in the patent literature. In particular, the reactivity of the azido group limits the applicability of the glycidyl azide polymers (GAP). The azide causes problems during the curing of the energetic material and shortens the shelf-life of the resulting material. The results of this research demonstrated that a tetrazole substituted glycidyl azide polymer could be readily synthesized. The synthetic steps were straightforward and did not present any overwhelming difficulties. While the exotherms for the glycidyl tetrazole polymer derivative were not as large as the glycidyl azide polymer exotherm, the benefits with regard to processing and storage could overcome this energetic disadvantage.

In Chapter V, a group of energetic foams was synthesized. By means of urethane chemistry, the polymers synthesized in the previous chapters were used to generate these energetic foams. The hydroxyl end groups on the polymers made this particular phase of the research possible. In the study of energetic materials, the physical characteristics of the compounds are just as important as the energetic capabilities. Foams provide a unique medium for energetic materials. Although they are less dense than energetic materials such as ammonium perchlorate, foams offer a wide number of advantages. A

rigid foam could easily provide a solid support for a liquid energetic material. Military personnel could also easily apply foams in the field in canisters or in more traditional weapons. These foams illustrate how tetrazoles can be applied to nearly every energetic application. Their inherent tunability opens up a large number of possible uses and applications.

In Chapter VI, energetic ionic liquids were designed and synthesized. Ionic liquids are molten salts that exhibit no detectable vapor pressure. Many of the current energetic materials such as monopropellants are toxic and volatile. If an ionic liquid were used instead of the normally used hydrazine, volitilty would no longer threaten the workers who deal with the propellants. Two classes of tetrazole ionic liquids were discussed in this chapter, and one was synthesized and characterized. The structural modifications proved that the physical properties and energetic potential of these liquids could be effectively tuned. With additional theoretical work, it is anticipated that the most promising energetic counter-anion will be discovered. A number of possibilities exist and they are discussed in the final chapter of this thesis.

Energetic gels that included tetrazoles were also studied (Chapter VII). Gels, like ionic liquids and foams, enjoy several special advantages. Primarily, gels are thixotropic. A thixotropic substance is one that will flow if a shearing force is applied, but solidify when the force is removed. Therefore, gels will not spill out of a ruptured container, and will be easily cast into a rocket motor. In this chapter, the preparation of a two-dimensional polymer was reported. The energetic potential was low compared to the performance of the GAP, but the suggested structural modifications should positively impact the performance. The three-dimensional polymers were synthesized as well.

These experiments proved that the molecular weight and the degree of cross-linking influenced the physical characteristics of the gels. Additional work will be necessary to provide optimum systems with the desired physical and energetic characteristics.

The research results in this thesis demonstrate that tetrazole derivatives are a versatile and useful class of compounds for applications toward the development of new and novel energetic materials. Tetrazoles provide a stable alternative to the ubiquitous energetic azido group. Due to their stability, tetrazoles are suitable energetic candidates in gels, foams, ionic liquids, and polymers.

CHAPTER II

A NOVEL APPROACH TO THE GENERAL SYNTHESIS OF TETRAZOLES

Introduction

Research on the preparation of tetrazoles has been conducted for more than 50 years. A tetrazole moiety is a 5-membered cyclic ring containing 4 nitrogen atoms and a carbon. A general 5-substituted tetrazole is shown in Figure 2-1. Tetrazoles can be prepared from imidoyl chlorides, amidrazones, nitriles, nitrilium salts, and isonitriles (Gupa et al., 1999). All of these reactions require the use of either an organic or inorganic azide ($-N_3$) in the presence of a proton source. The most common method of producing tetrazoles is through the reaction of a nitrile with an organic azide. However, inorganic azides are easily converted to hydrazoic acid (HN_3) through protonation. Hydrazoic acid is extremely dangerous due to its explosive nature and high toxicity and, for this reason, reactions with azide must be conducted with extreme caution. For these reasons, researchers have tried to develop alternate methods for the preparation of tetrazoles. As a consequence, the focus of this research was to develop safe and efficient methods for the preparation of tetrazoles that improved upon the current techniques. The goal was to develop a process that used sodium azide while limiting the possibility of forming the toxic and explosive hydrazoic acid. Scalability was also a concern throughout this project.

Tetrazoles and their derivatives have a wide number of applications. Primarily, tetrazoles are used as rocket propellants (Brown, 1967), primary explosives (Tarver et al., 1967; Henry, 1963), and as pharmaceutical precursors in medicinal chemistry (Bradbury

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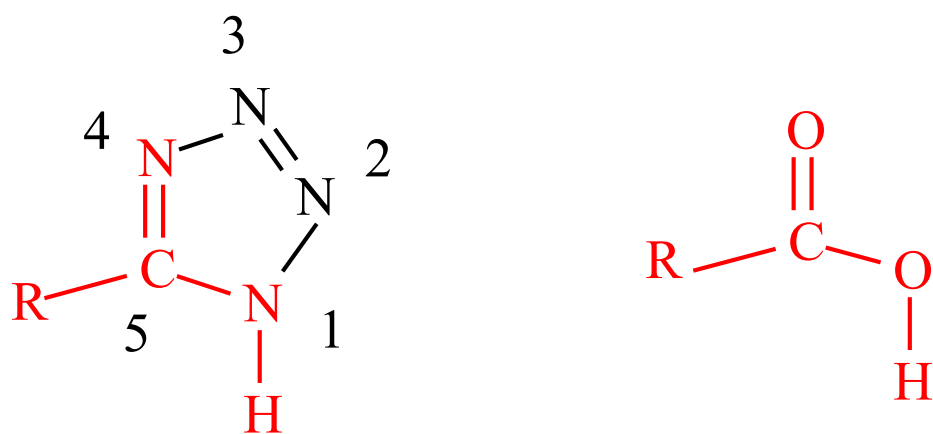
Figure 2-1.   Structural comparison of the carboxylic acid type moiety present in the tetrazole ring.

et al., 1993; Carini, 1991; Duncia et al., 1991; Koyama et al., 1987; Raman et al., 1980; Rossano, 1992; Larson et al., 1994; Singh et al., 1989; Stenberg et al., 1984). Tetrazoles exhibit potential biological activity because the tetrazole ring is considered a biomimic of the carboxylic acid functional group (Figure 2-1). However, the tetrazole moiety is metabolically more stable than the carboxylic acid group (Gupta, et al., 1999). This special characteristic suggests that tetrazoles will continue to have a significant impact in pharmaceutical research.

Currently, there is a new class of drugs that shows great potential for successfully treating hypertension. These angiotensin-II-antagonists or receptor blockers (AT-II blockers) all possess a tetrazole moiety (Bradbury et al., 1993; Larsen et al., 1994). AT-II blockers were originally developed as an alternative to the commercially successful ACE-inhibitors. The ACE-inhibitors exhibited a number of negative side effects. Both classes of these drugs act on the rennin angiotensin system (RAS), which is a key element in blood pressure regulation. AT-II antagonists have great potential, but they suffer one large drawback—the most efficient method used to produce tetrazoles involves the use of sodium azide.

Sodium azide is used in air bag inflation, pharmaceuticals, and as an intermediate in explosive manufacturing. Sodium azide is highly toxic by inhalation in aerosols, ingestion, or skin absorption; and, it forms dangerous explosive heavy metal azides in laboratory equipment and drain traps.

Hydrazoic acid is believed to be the ultimate toxic agent in humans exposed to sodium azide. NaN_3 is rapidly converted to HN_3 on contact with moisture (National Research Council, 1981). The acute toxicity of sodium azide is very high. Symptoms of

exposure include lowered blood pressure, headache, hypothermia, and (in cases of serious overexposure) convulsions and death. Ingestion of 100 to 200 mg in humans may result in headache, respiratory distress, and diarrhea. Target organs are primarily the central nervous system and brain. Symptoms of acute exposure to hydrazoic acid include eye irritation, headache, dramatic decrease in blood pressure, weakness, pulmonary edema, and collapse. Solutions of sodium azide can also be absorbed through the skin. When solutions of hydrazoic acid are formed, the highly toxic gas can easily evaporate and cause a serious inhalation hazard.

While sodium azide is not explosive under normal conditions or considered a flammability hazard, it is commonly used in detonators and other explosives. It does impose explosion risks when shocked or heated to high temperatures. Violent decomposition can occur when heated to 275 ^{o}C. The decomposition products are nitrogen and sodium oxides. The toxicity and explosive dangers associated with azide illustrate why it is important to develop methods for tetrazole preparation that reduce or even eliminate its use.

As mentioned previously, there are many ways to prepare tetrazoles from different starting materials. Most of these methods involve the use of azides. Their preparation from nitriles commonly involves the use of an amine hydrochloride and sodium azide. In one case, hydrazoic acid (HN_3) is complexed as its amine salt by the reaction of ammonium chloride and sodium azide in polar, high-boiling solvents such as dimethylformamide and methylsulfoxide (Benson, 1967; Butler, 1977; Herbst and Wilson, 1957; Finnegan *et al.*, 1958; Kabada, 1973). Recently, several different 5-substituted tetrazoles were prepared from nitriles using sodium azide and an excess of

triethylamine hydrochloride in aromatic solvents (Koguro *et al*., 1998). Another method has been reported where nitriles react with sodium azide and a stoichiometric amount of acetic acid in *tert*-butyl alcohol (Russell and Murray, 1993). Extreme care must be taken with these types of reactions to monitor any possible HN_3 in the headspace of the reactor to avoid explosive levels of hydrazoic acid.

Several other methods exist for the preparation of tetrazoles from nitriles where dangerous levels of hydrazoic acid can be avoided. The use of trialkyltin azide (Duncia *et al*., 1991) or trialkylsilylazide in conjunction with either dialkyltin oxide (Wittenberger and Donner, 1993) or trimethylaluminum (Huff and Staszak, 1993) has been reported but each suffers from a difficult initial reagent synthesis. These systems using tin lead to problematic separations of tin from the product and involve careful handling of toxic tin. Systems containing trimethylaluminum include laborious catalyst neutralization and waste disposal as well as careful handling due to moisture sensitivity. A method using tetramethylguanidinium azide (Papa, 1966) has been reported but suffers from dangerous reagent synthesis involving the direct use of HN_3. The use of a surfactant in conjunction with ammonium chloride and sodium azide (Jursic and LeBlanc, 1998) has been developed but is limited due to long reaction times in excess of 5 days.

The limitations that exist for these systems must be avoided if a safe and economical process is to be developed for the preparation of tetrazoles. Therefore, the objective of this project was to design a system that permitted the formation of tetrazole derivatives from a nitrile using azide while reducing the potential to create significant levels of hydrazoic acid. The reactions reported in this chapter were run with the intent of finding a simple process that minimized the possibility of hydrazoic acid formation,

produced high yields, used azide as the limiting reagent, and allowed for the recycle of all components of the reaction system.

Experimental Methods

Materials

The chemicals used during these investigations were obtained and used without further purification. These include the following: benzonitrile (Aldrich, 99%), benzyltriethylammonium chloride (Aldrich, 99%), butyldiethylamine (Aldrich, 99%), butyldimethylamine (Aldrich, 99%), heptane (Aldrich, 99%), hydrochloric acid (Aldrich, 37%), methanol (Aldrich, 99.8%), 5-phenyl-1*H*-tetrazole (Aldrich, 99%), sodium azide (Aldrich, 99%), tributylamine (Aldrich, 99%), triethylamine (Aldrich, 99.5%), triethylamine hydrochloride (Aldrich, 98%), trioctylamine (Aldrich, 99%), triphenylmethyl chloride (Aldrich, 98%), tripropylamine (Aldrich, 99%).

Procedure

All the reaction procedures described below were performed in a 100ml single neck (24/40) round bottom flask. Once the reactants were loaded, the reaction flasks were all flushed with argon for 1 minute and left under argon for the duration of the reaction. All reactions were stirred at the same rate using a teflon coated magnetic stir bar. All reactions were heated using a silicon oil bath and reaction flasks were fitted with a reflux condenser. Sodium azide was the limiting reagent in all reactions so mol percentages and other references to relative added quantities were all based on the amount of added sodium azide. All reactions were followed by the same post-reaction

product isolation (work up) procedures unless otherwise noted. For 5-phenyl-1*H*-tetrazole, mp=216-217°C, ^{1}H, δ (CDCl$_3$): 7.62 (m, 3H), 8.05 (m, 2H). These data corresponded to the literature values for the melting point of 5-phenyl-1H-tetrazole, mp=215-217°C and the NMR spectra (Koguro, 1998).

(Figure 2-3) Sodium azide (2.25g, 35mmol) was first weighed into the reaction flask and clamped into the hood. Benzonitrile (~5ml) was added followed by triethylamine hydrochloride (4.9g, 35mmol) and the remaining benzonitrile (15ml).

(Synthesis of ammonium hydrochloride salts). The amine hydrochloride (10g) was placed into a 1 L round bottom reaction flask. The flask was clamped into the hood and lowered into an ice bath. Diethylether was added and a magnetic stir bar was used to stir the mixture. Dry HCl in ether was then added via syringe. The resulting crystals were collected via vacuum filtration and stored under reduced pressure for 24 hours. The crystals were stored in a desiccator. The products were analyzed via ^{1}H NMR. Diethylbutylamine HCl, ^{1}H, δ (CDCl$_3$): 0.98 (t, 3H), 1.40 (m, 2H), 1.82 (m, 2H), 2.01 (d, 6H), 2.86 (m, 4H), 3.02 (m, 2H); Dimethylbutylamine HCl, ^{1}H, δ (CDCl$_3$): 0.98 (t, 3H), 1.40 (m, 2H), 1.82 (m, 2H), 2.81 (d, 6H), 3.02 (m, 2H); Tributylamine HCl, ^{1}H, δ (CDCl$_3$): 0.98 (t, 9H), 1.42 (sextet, 6H), 1.75 (m, 6H), 3.05 (m, 6H); Tripropylamine HCl, ^{1}H, δ (CDCl$_3$): 1.01 (t, 9H), 1.84 (m, 6H), 2.95 (m, 6H).

(Figure 2-6) Synthesis of 5-phenyl-2-triphenylmethyl tetrazole. To a 250mL round bottom flask 2.25g (35mmol) of sodium azide was added. Benzonitrile (5mL) was

then introduced to cover the solid. A stoichiometric amount of quaternary ammonium salt was then added to the flask, followed by more benzonitrile (15mL). A magnetic stir bar was added and a condenser was attached. The system was then flushed with nitrogen and sealed. After the reaction was complete, the condenser was removed and the reaction remained in the hot oil bath. Then a stoichiometric amount of trityl chloride in hot benzonitrile was added dropwise via pipette. The system was then resealed with the condenser and allowed to stir. The reaction was then cooled on ice and water (40mL) was introduced. Cold heptane (150mL) was then added to precipitate the product. The entire flask was then sealed with a rubber stopper and placed under refrigeration for at least 24 hours. The crystals were then filtered, washed with water, and collected with ethyl acetate. The ethyl acetate was reduced with a rotary evaporator and all excess solvents were removed from the product crystals in an oven (65°C) under reduced pressure. Mp= 155-156°C, 1H δ (CDCl$_3$): 7.08-7.48 (m, 18H), 8.03 (m, 2H) These values corresponded to those found in the literature (Myznikov, 2002).

(Figure 2-8) Sodium azide (2.25g, 35mmol) was first weighed into the reaction flask and clamped into the hood. Benzonitrile (~5ml) was added followed by a stoichiometric amount of benzyltriethylammonium chloride (8.0g, 35mmol). The proton source (triethylamine hydrochloride, TEAHC (0.49g, 3.5mmol, 10 mol%) or triethylammonium 5-phenyltetrazolate, TEAPT (5ml of 0.7M solution, 3.5mmol, 10 mol%)) was then added followed by the remaining benzonitrile (~15ml for reactions with TEAHC and ~10ml for reactions with TEAPT).

Preparation of 0.7M solution of triethylammonium 5-phenyltetrazolate (TEAPT) in benzonitrile (Figure 2-7):   1.02g of 5-phenyl-1*H*-tetrazole was weighed into a 10ml volumetric flask.   A few milliliters of benzonitrile were added followed by a stoichiometric amount of triethylamine (relative to the weighed 5-phenyl-1*H*-tetrazole) via microsyringe. As soon as the solid was dissolved the solution was diluted to the 10ml mark with benzonitrile to give a molarity of ~0.7M.

(Gaseous Workup) To a 250mL three-neck round bottom flask was added 2.25g (35mmol) of sodium azide. Benzonitrile (~5mL) was then introduced to cover the solid. A stoichiometric amount of amine hydrochloride was then added to the flask, followed by more benzonitrile (~15mL).   A magnetic stir bar was added and a condenser was attached. The system was then flushed with nitrogen and sealed. After the reaction was completed, the flask was removed from the hot oil bath and placed on ice while stirring. The condenser was removed and the center neck was sealed. The flask was then fitted with a sidearm attachment connected to a gas bubbler and a glass tube to bubble the HCl gas through the solution. The HCl gas was then bubbled into the mixture with the aide of argon. The product crystals were then filtered and the filtrate was collected in a 100mL round bottom flask. Azide and a stir bar were then added to the filtrate and the reaction was allowed to continue. The crystals from both cycles were filtered, washed with water, and collected with acetone and placed in an oven (65°C) under reduced pressure.

<u>Results and Discussion</u>

The focus of this research was to develop a system for preparing tetrazoles using a nitrile and sodium azide in which the potential for hydrazoic acid formation could be reduced, controlled or even eliminated. Benzonitrile was chosen as the initial substrate because its product tetrazole, 5-phenyl-1*H*-tetrazole, is a valuable precursor to many pharmaceuticals. Initial experiments used toluene as a solvent in the presence of sodium azide, benzonitrile and tetrabutylammonium chloride (TBAB). TBAB is a very commonly used commercially available phase-transfer catalyst (PTC).

Phase transfer catalysis is a special technique that appeared to offer several benefits to this project. A phase transfer catalyst is typically an ammonium salt with long alkyl chains. The catalyst forms a reactive species with a reactive salt such as KCN or NaN$_3$. The long greasy alkyl chains transfer the reactive species into the organic phase containing the starting material (Liotta et al., 1990). The reaction then takes place when the entities are brought together in the organic phase.

For this project, it was believed that PTC would transfer the reactive azide anion into the toluene phase for reaction with benzonitrile. Several different sets of reaction conditions were tested. The temperature, reactant concentration, and catalyst amount were all systematically adjusted. While these variations were tested, it was decided to use the benzonitrile as both the solvent and reactant. In all cases, these reactions were found to be largely unsuccessful as no product tetrazole was produced.

The literature was extensively reviewed and it was determined that the presence of a tertiary amine hydrochloride might facilitate the reaction. Ammonium salts of azides in which the ammonium salt contained at least one proton have been reported to be

successful reagents for the [3 + 2] cycloaddition reactions with nitriles (Koguro et al., 1998). However, ammonium salts without a proton (PTCs) did not facilitate reaction. Therefore, it was proposed that a modified version of a phase-transfer catalyst should be used. A protonated tertiary amine was used instead of a traditional quaternary ammonium salt. The modified PTC still contained enough organic character to transfer the reactive azide anion and, consistent with the interpretation of the literature, the presence of the proton would aid in the cycloadditon reaction between the azide and benzonitrile by forming the reactive species show in Figure 2-2. Because triethylamine hydrochloride (TEAHC) was commercially available, it was chosen as the initial amine hydrochloride. The reaction for this particular system is shown in Figure 2-3.

This reaction was initially attempted at room temperature in order to keep the reaction conditions relatively mild. The presence of a stoichiometric amount of TEAHC (relative to sodium azide) made safety an important concern because all of the sodium azide could have been transformed into hydrazoic acid under the conditions of the experiment. At room temperature, this reaction produced an isolated yield of 20 % in 24 hours. Therefore, the reaction was heated slightly to 50 $^{\circ}$C and run for 24 hours. These conditions produced an isolated yield of 97%. Reactions were found to go to completion only when TEAHC was used in equimolar quantities relative to the sodium azide. Due to the success of this reaction, the experiment was repeated at shorter times to verify when the reaction was complete. Figure 2-4 presents a graph showing the isolated yields of 5-phenyl-1H-tetrazole versus time at 50°C for the reaction system shown in Figure 2-3. This graph illustrates that the reaction appears to be complete within 16 hours. The reaction was also attempted at 100°C with similar results. At this higher temperature,

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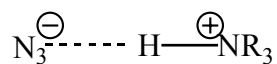
Figure 2-2.   The complex between azide ion and a protonated tertiary
               amine.
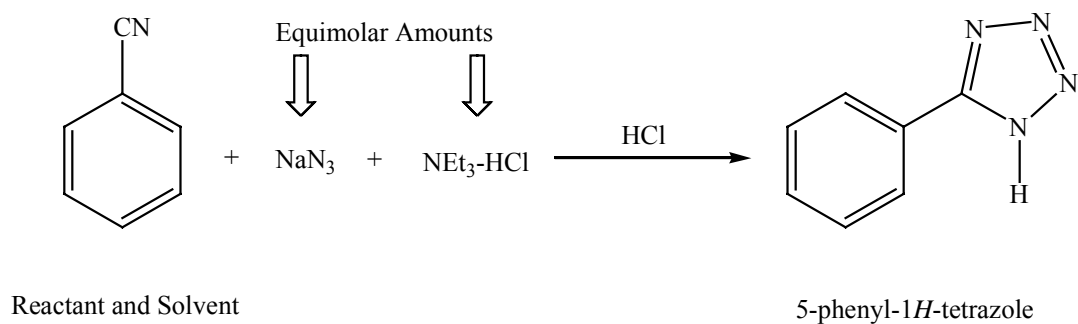
Figure 2-3.   General reaction between triethylamine hydrochloride and sodium
               azide with benzonitrile as both solvent and reactant in the
               preparation of 5-phenyl-1*H*-tetrazole.

Figure 2-4. Isolated yields of 5-phenyl-1*H*-tetrazole versus time for the reaction shown in Figure 5-2 at 50°C.
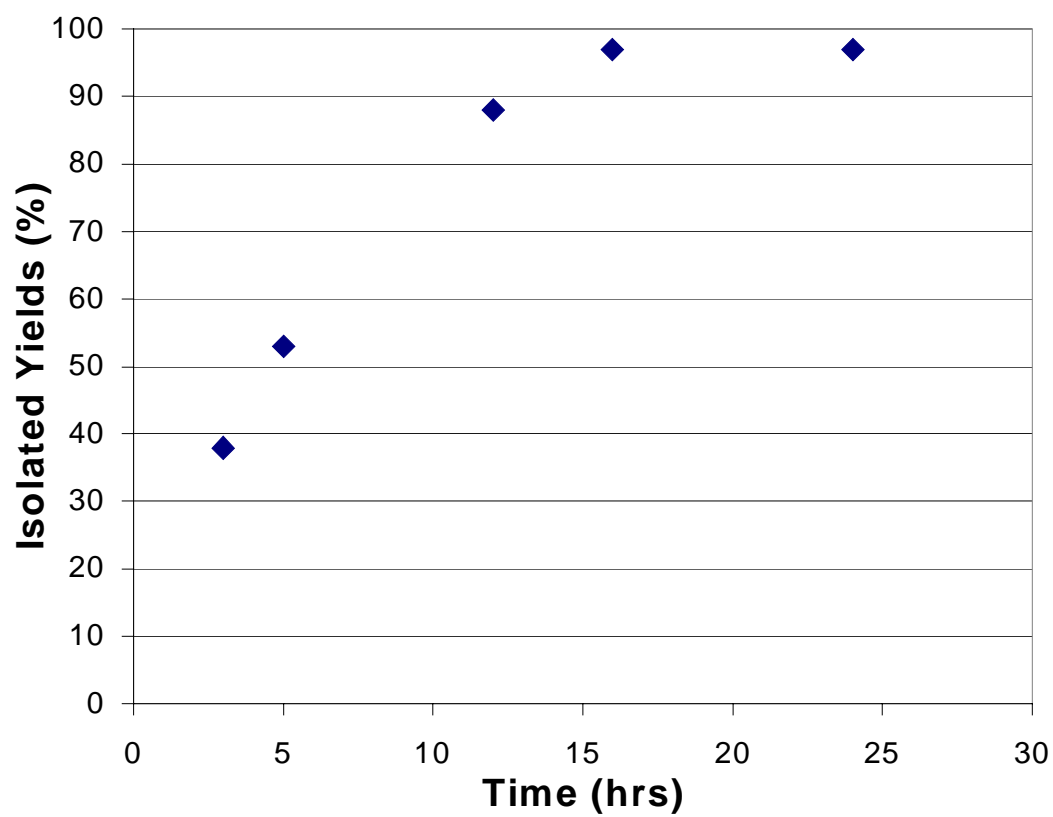
however, an isolated yield of 97% was obtained after only 1 hour. The amine hydrochloride was used without purification. It should be noted that the drying and crushing of the amine hydrochloride had a negligible effect on the overall isolated yields.

In addition to TEAHC, a number of other proton sources were tested. These included tripropylamine hydrochloride, butyldiethylamine hydrochloride, butyldimethyl hydrochloride, tributylamine hydrochloride, and trioctylamine hydrochloride (Figure 2-5). The analysis of these new proton sources was driven by two motives. The first was to determine whether TEAHC was indeed the most effective, and the second was to find a proton source that was soluble in benzonitrile. This characteristic would allow the amine hydrochloride to be recycled if a gaseous HCl workup was used in lieu of the standard aqueous workup. With the aide of gaseous HCl, the product could be precipitated and filtered while the proton source remained active and soluble in the benzonitrile. The beauty of this process lied in the fact that only the addition of sodium azide to the solvent (benzonitrile) containing the recycled amine hydrochloride would be needed to conduct another reaction.

The first amine hydrochloride tested was the long chained trioctylamine hydrochloride. This species was soluble in benzonitrile, but yielded no product. It was hypothesized that the steric exposure of the protonated nitrogen played a key role in the effectiveness of the amine hydrochloride in the formation of the reactive species (Figure 2-2). The shorter, assymetrical amine hydrochlorides were then tested with the hope of finding an effective proton source with a sterically exposed nitrogen and enough organic character to remain soluble in benzonitrile. Indeed, these catalysts proved to be soluble in benzonitrile and they produced varying yields of tetrazole as seen in Table 2-1.
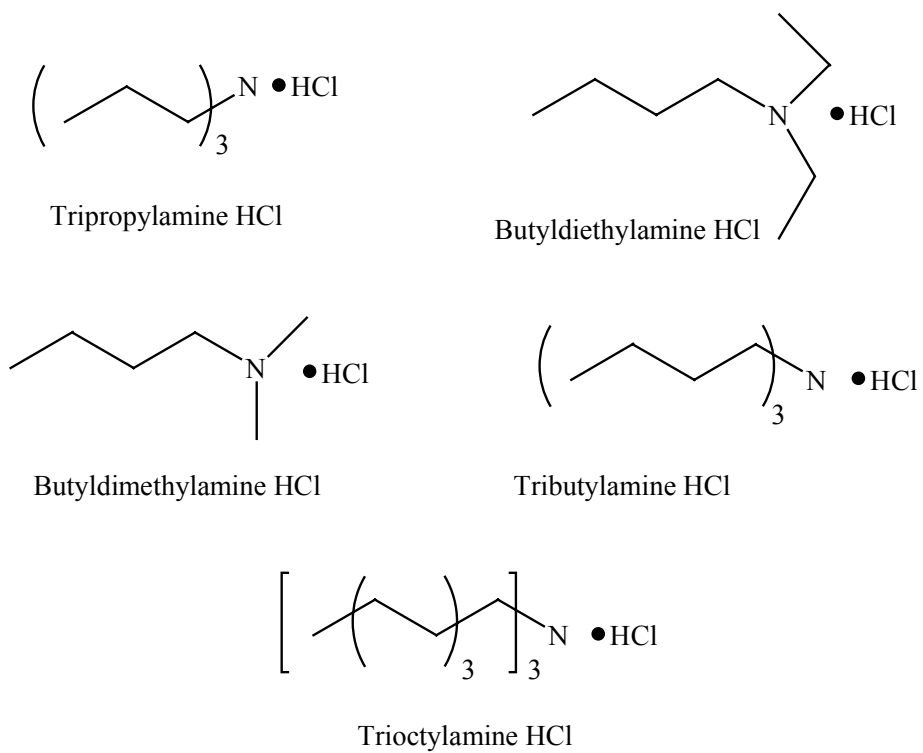
Figure 2-5.   Tertiary amines employed as proton sources in the formation of the tetrazole functionality.

Table 2-1.   Yields of tetrazole as a function of time and temperature.

Proton Source	Time(hours)	Temp. (°C)	Yield (%)
Tripropylamine HCl	24	50	60
	1	100	75
	2	100	86
	4	100	91
Butyldiethylamine HCl	24	50	85
	1	100	74
	2	100	79
	4	100	90
Butyldimethylamine HCl	24	50	82
	2	100	62
	4	100	60
	8	100	76
Tributylamine HCl	24	50	74
	5	100	57
	24	100	50
Trioctylamine HCl	24	50	0

In all of the reactions that used a soluble amine hydrochloride, gaseous HCl was used to precipitate the product. After filtering the product and washing with benzonitrile, NaN_3 was added to the filtrate and the procedure was repeated. A list of the results from these consecutive recycle experiments is in Table 2-2. These experiments were a success. By using a soluble amine hydrochloride, the product was successfully isolated without destroying the catalyst with a traditional aqueous wash. From the standpoint of economics, this process represented an important breakthrough.

In addition to the reactions that used a stoichiometric amount of the amine hydrochloride, several experiments were run with a 2:1 addition (relative to azide). While the ability to recycle the amine hydrochloride made this method economically acceptable, the excess addition had little effect on the isolated yields. The reactions run with tripropylamine hydrochloride only displayed a 1-4% increase in isolated yields when a 2:1 ratio was used. Overall, tripropylamine hydrochloride clearly provided the best results with the gaseous HCl workup. However, headspace analysis of the reaction with tripropylamine hydrochloride showed that 4-5% of the NaN_3 was converted to hydrazoic acid during the course of the reaction. In contrast, triethylamine hydrochloride did not produce any detectable hydrazoic acid regardless of the temperature of the reaction. Therefore, the addition of a 2:1 amount (relative to azide) of the amine hydrochloride did little to improve this process. It was concluded that it would not be advisable to use larger than stoichiometric quantities of the proton source.

As an extension to this novel system, the *in situ* protection of the tetrazole moiety was investigated. To provide more advanced intermediates--especially those that are precursors for AT-II receptor antagonists--the tetrazole moiety is commonly protected

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Table 2-2.   Yields of tetrazole between the first and second cycle.

Proton Source	Time (Hours)	Temp. (°C)	Yield of 5PT (%)*
Tripropylamine HCl	4	100	91/89
Butyldiethylamine HCl	24	50	85/84
Butyldimethylamine HCl	24	50	89/88
Tributylamine HCl	24	50	74/74

*(Yield of First Cycle/Yield of Second Cycle)

(Larson *et al*., 1994; Carini *et al*., 1991; Lo and Rossano, 1992; Schuman *et al*., 1991). This is accomplished through a separate synthetic step by adding a triphenylmethyl group to the N-2 position of the tetrazole ring. The protection step involves reaction of the tetrazole moiety with triphenylmethyl chloride (trityl chloride) in the presence of tertiary amine as base. Because the reaction system under investigaion was believed to already contain a deprotonated tetrazole ring at the end of reaction prior to acidification, it was proposed that the simple introduction of trityl chloride should provide the desired protected product. Figure 2-6 shows the synthetic steps involved for the protection of the tetrazole ring with trityl chloride.

In order to optimize the isolation of the protected product, the trityl chloride was added to the reaction at various temperatures (0-115°C) using a variety of methods; and, allowed to react for several hours (0-16). Most commonly, the trityl chloride was dissolved in benzonitrile or a mixture of benzonitrile and heptane. Originally, the solution was mixed at 25°C and a great deal of benzonitrile was needed to dissolve the trityl chloride. For every 10g of trityl chloride, nearly 45 mL of benzonitrile was required to fully dissolve the solid. This led to an undesirable dilution effect that hindered the efficiency of the reaction. The yields of protected tetrazole ranged from 61-67% when the trityl chloride solution was mixed and added at 25°C regardless of the other variables.

Therefore, the solutions were heated to increase the solubility of the trityl chloride. At 70°C, 10g of trityl chloride dissolved in only 10 mL of benzonitrile. While trityl chloride melts at 109°C, its addition as a liquid at 115°C did not produce an acceptable result. This was also true for a neat addition of trityl chloride at 50°C. Based on

Ph—C≡N   + $\overset{\ominus}{Cl}$ $\overset{\oplus}{H}$-NEt$_3$ $\xrightarrow{\text{NaN}_3}$ Ph—⟨tetrazolate⟩   +   NaCl

Ph—⟨tetrazolate·H-NEt$_3$⟩   +   Cl-C(Ph)$_3$ ⟶   Ph—⟨tetrazole⟩—C(Ph)$_3$
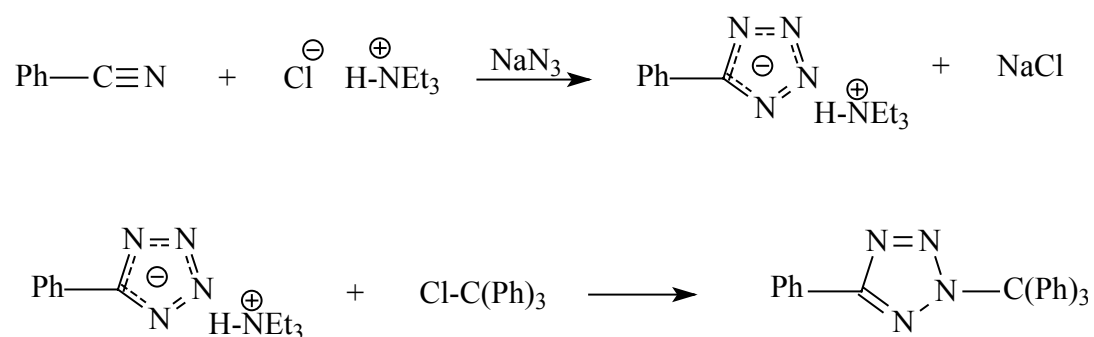
Figure 2-6.   Reaction sequence showing the formation of triethylammonium 5-phenyltetrazolate and subsequent tetrazole ring protection by reaction with triphenylmethyl chloride.

all of the experiments, it was realized that 70°C was the ideal temperature for the addition of trityl chloride dissolved in benzonitrile. These results are shown in Table 2-3.

A series of experiments were run to substantiate the yields obtained in the above reactions. In these experiments, 5-phenyl-1H-tetrazole was dissolved in benzonitrile and deprotonated with triethylamine. The trityl chloride was then added and the product was extracted with heptane. The independent yield from this step was 85%. Overall yields near 80% were obtained for most of these reactions. These yields were consistent with the results obtained in the one-pot reaction process described previously if one assumed that the initial tetrazole formation reaction went to ~93-97% completion (as clearly demonstrated earlier in this chapter).

A mechanism, consistent with the experimental observations, was proposed to describe the formation of the tetrazole derivative (Figure 2-7). The TEAHC had a high solubility in the benzonitrile phase and was believed to form a complex on the surface of the solid sodium azide particles. The formation and reaction of species of this type on the surface of solid salt particles is described in the literature (Liotta, 1987). This complex then underwent an ion-exchange process to form solid sodium chloride and a soluble species (N_3^-•••H-NEt$_3^+$) believed to be the reactive species for the cycloaddition. Hydrogen-bonded complexes of this type (between HN_3 and different bases) have been well studied through the use of infrared spectroscopy and proton nuclear magnetic resonance spectroscopy (Nelson, 1970; Lieber et al., 1963; Nelson et al., 1970). In order to possibly speed up the overall rate of reaction, a quaternary ammonium salt, benzyltriethylammonium chloride (BTEAC), was introduced into the system. This was expected to aid in the transfer of the azide anion into the organic phase (where a high

Table 2-3.   The yield of protected tetrazole as a function of initial addition
            temperature.

Temp. of Reaction During Addition (°C)	Time Trityl Chloride Reacted (Hours)	Temperature (°C)	Yield of Protected 5PT (%)
0	3	100	77
100	3	100	81

*All of these reactions used TEAHCl for the first step

$$NaN_3 \text{ (s)} + Et_3\overset{\oplus}{N}H\ \overset{\ominus}{Cl}\text{ (soln)} \rightleftharpoons \overset{\oplus}{Na}\ \overset{\ominus}{N_3}\ \bullet\overset{\oplus}{H}NEt_3\overset{\ominus}{Cl}\text{ (surface)} \qquad (1)$$

$$\overset{\oplus}{Na}\ \overset{\ominus}{N_3}\bullet\ \overset{\oplus}{H}NEt_3\overset{\ominus}{Cl}\text{ (surface)} \rightleftharpoons NaCl \text{ (s)} + \overset{\ominus}{N_3}\cdots H-\overset{\oplus}{N}Et_{3\text{(soln)}} \qquad (2)$$

$$(3)$$
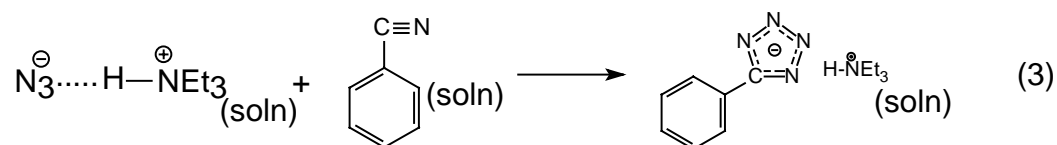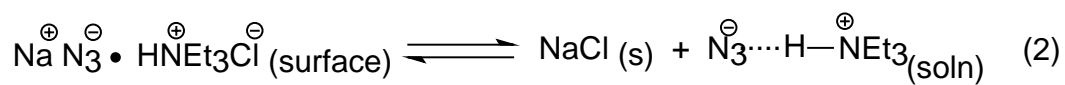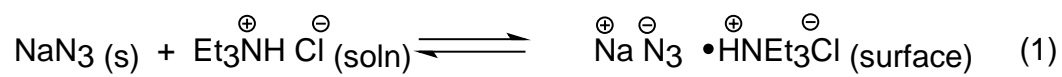
Figure 2-7.   Proposed mechanism for the reaction shown in Figure 2-3.

concentration of the TEAHC existed) and facilitate a faster formation of the reactive complex. Table 2-4 shows a comparison of the results achieved with and without the BTEAC present. For the 5 hour reactions, the isolated yield increased almost 20% in the presence of BTEAC. However, the 12 hour reaction produced a lower isolated yield with the BTEAC.

In Figure 2-7, the resulting product in step 3 was a complex between the tetrazolate anion and a protonated triethylamine cation. It was proposed that if a quaternary ammonium cation could form a more stable complex with the tetrazolate anion, the protonated triethylamine could ion exchange with a quaternary ammonium chloride to regenerate the reactive species (N_3^-••••H-NEt_3^+) for continuous reaction. It was expected that a system containing a stoichiometric amount of quaternary ammonium chloride salt (to complex each mole of tetrazolate product formed) and a less than stoichiometric amount of triethylamine hydrochloride would facilitate a catalytic reaction. This proposed reaction sequence is shown in Figure 2-8.

This reaction system was initially setup and run with a stoichiometric amount of BTEAC and only a 10 mol% of proton source, TEAHC. The conditions were varied and the results are depicted in Table 2-5. A 71% isolated yield of the product was achieved in 48 hours at 50°C using only a 10 mol% of TEAHC. Accordingly, only 10 mol% of the azide could potentially form hydrazoic acid. However, if the quaternary ammonium cation was indeed responsible for stabilizing the deprotonated tetrazolate anion species, less than a stoichiometric amount of BTEAC would result in a poor isolated yield. This result would occur because the TEAHC would not undergo the ion exchange that continued the reaction. When only a 10 mol% of BTEAC and TEAHC were used, an

Table 2-4.   Comparison of isolated yields for the reaction shown in Figure 2-3 at 50°C with and without BTEAC. Mol percentages are relative to sodium azide addition.

BTEAC (mol%)	NEt$_3$ • HCl (mol%)	Time (hours)	Isolated Yield (%)
	100	5	53
	100	12	88
10	100	5	71
10	100	12	78
100	10	48	71
10	10	48	4
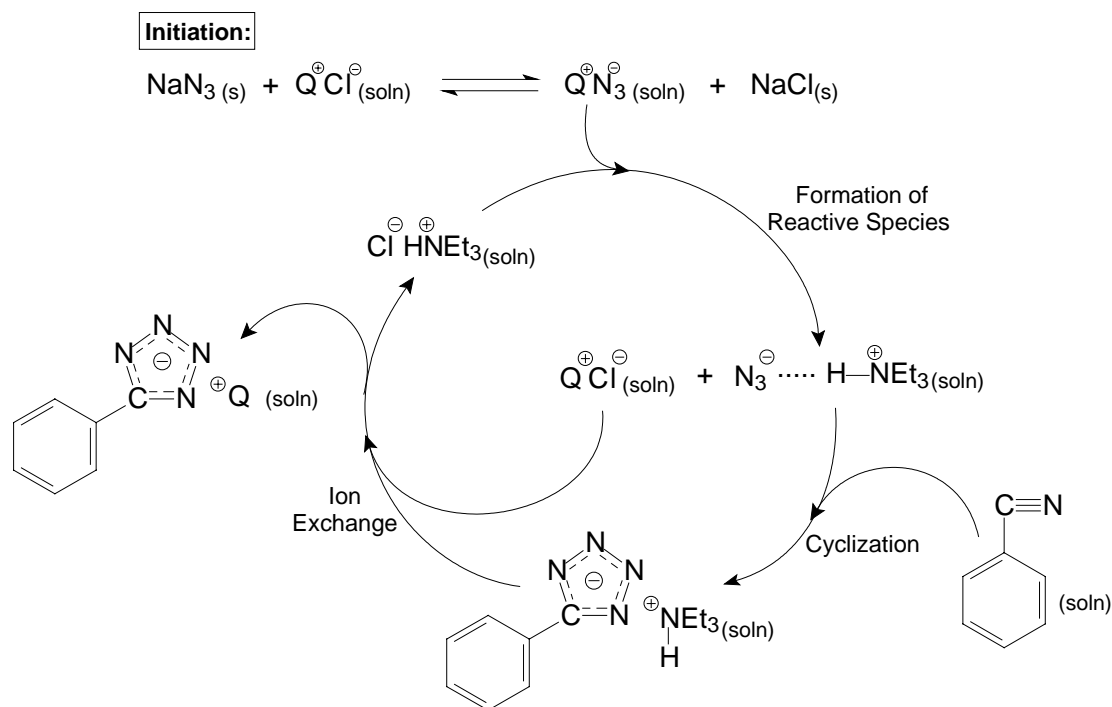
Figure 2-8.   Proposed catalytic cycle for the preparation of 5-phenyl-1H-tetrazole using a stoichiometric amount of triethylamine hydrochloride (TEAHC) and a 10 mol% of benzyltriethylammonium chloride (BTEAC).

Table 2-5.   The results from the temperature, time, and mol% of TEAHC
variations. In all of these experiments, a stoichiometric amount of
BTEAC was used.

Mol % of TEAHC	Time (hrs)	Temp. (°C)	Yield of 5PT(%)
5	48	50	41
10	48	50	71
20	48	50	75
30	48	50	71
40	48	50	61
5	72	50	65
10	72	50	79
50	72	50	88
10	1	100	47
10	2	100	52
10	3	100	65
10	6	100	70
5	24	100	60
10	24	100	62
20	24	100	69
50	24	100	79

isolated yield of only 4% was obtained. Therefore, the proposed catalytic mechanism shown in Figure 2-8 was believed to be a valid representation of this system.

The first step of the proposed catalytic cycle (Figure 2-8) was an initiation step in which the quaternary ammonium chloride shuttled the azide anion into the organic phase. Here, the azide reacted with TEAHC, the proton source, to provide the reactive species and the original quaternary ammonium chloride. The reactive species then reacted with the nitrile to give the product. Next, an ion exchange step stabilized the product tetrazole with the quaternary ammonium cation. The ion exchange step also regenerated the triethylamine hydrochloride proton source for further reaction. As stated earlier, if less than a stoichiometric amount of quaternary ammonium salt was used, the reaction was limited by the ion exchange step. Of great interest in this cycle was the fact that after the cycloaddition step, the product tetrazolate species was being stabilized by a protonated triethylamine. Therefore, it was proposed that this species (the triethylammonium 5-phenyltetrazolate, TEAPT) could serve as the catalyst in the system instead of triethylamine hydrochloride.

The use of the product tetrazole as the proton source was investigated next. As shown in Figure 2-9, 5-phenyl-1H-tetrazole is insoluble in benzonitrile. However, it is soluble when deprotonated with a stoichiometric amount of triethylamine. It is known that the limited solubility of tetrazoles in many organic solvents is due to the intermolecular hydrogen bonding that exists (Gupta, 1999) as shown in Figure 2-10. This H-bonding system breaks down with the addition of triethylamine due to deprotonation. Reactions were performed using a 10 mol% of the TEAPT species as the proton source with benzonitrile as reactant and solvent in the presence of sodium azide and a
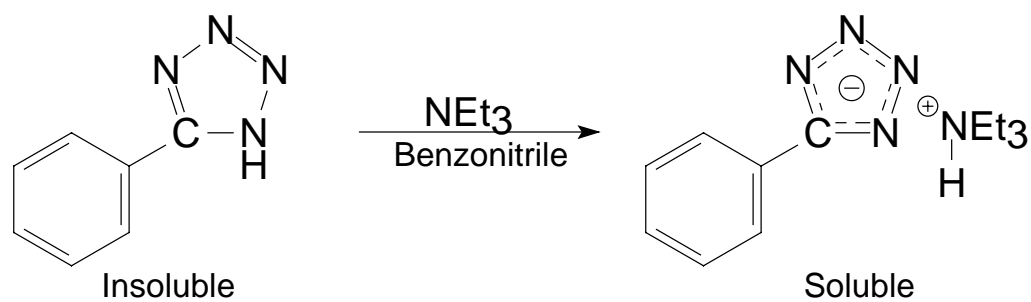
Figure 2-9.   Reaction showing the deprotonation of the 5-phenyl-1H-tetrazole
to produce a soluble triethylammonium 5-phenyltetrazolate
species (TEAPT).
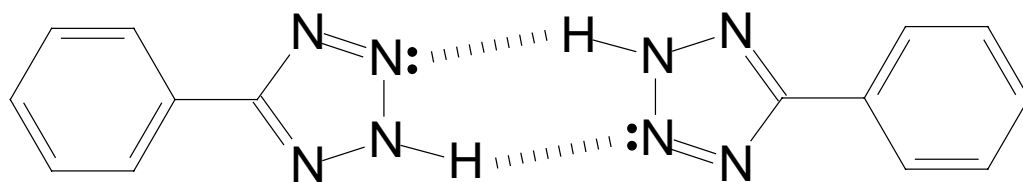
Figure 2-10.   Intermolecular hydrogen bonding of 5-Phenyl-1*H*-tetrazole.
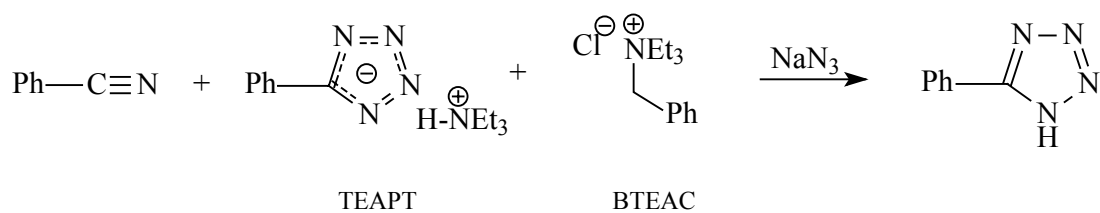
Figure 2-11.   Reaction scheme using 10 mol% TEAPT as the proton source.

stoichiometric amount of BTEAC as shown in Figure 2-11. No product was formed when sodium azide was reacted with only benzonitrile at 50 $^{\circ}$C for 48 hours. When this reaction was repeated in the presence of a 10 mol% of TEAPT, again, no product was formed. When sodium azide was reacted with benzonitrile only in the presence of a stoichiometric amount of BTEAC (no TEAPT) at 50 $^{\circ}$C for 48 hours a 15 % isolated yield of the product was obtained. But when the sodium azide was reacted with benzonitrile in the presence of both a stoichiometric amount of BTEAC and a 10 mol% of TEAPT an isolated yield of 87% is achieved. A proposed catalytic cycle for this system is shown in Figure 2-12.

Again, the quaternary ammonium cation transferred the azide anion into the organic phase during the initiation step. This azide underwent an ion exchange with the TEAPT/TEAHC to produce a stabilized product and the reactive species. This reactive species then reacted with benzonitrile to regenerate the TEAPT/TEAHC species for further catalytic reaction. This novel system provided direct control over the potential amount of hydrazoic acid that can form in the system. By only introducing a catalytic amount of proton source, there could never be more than an equivalent amount of hydrazoic acid present at any given time. This reaction, as shown by the results in Figure 2-12, did not proceed without a stoichiometric amount of BTEAC even when a 10 mol% of TEAPT was present. Therefore, it was believed the quaternary ammonium cation was imperative for stabilization of the tetrazolate anion while freeing up the protonated triethylamine for further reaction.
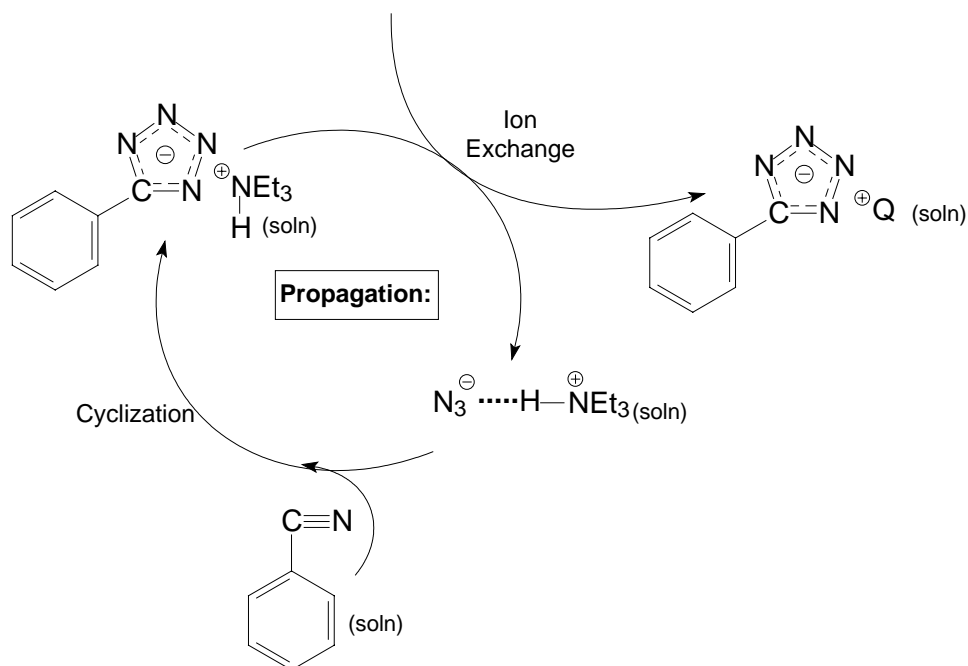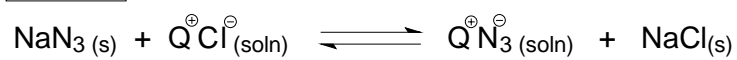
Figure 2-12.   Proposed catalytic cycle for the reaction shown in Figure 2-11.

Conclusions

Two novel systems that use benzonitrile as reactant and solvent for the preparation of 5-phenyl-1*H*-tetrazole were developed. The first system used a modified version of phase-transfer catalyst (a protonated tertiary amine) in stoichiometric amounts relative to sodium azide. This system was run at the relatively mild temperature of 50 °C and provided an isolated product yield of 97% within 16 hours. It was also demonstrated that a protected tetrazole can be prepared *in situ* prior to acidification with the addition of trityl chloride. This would allow for subsequent derivatization of other functionalities without interference of the tetrazole moiety.   The second system demonstrated the ability to control the potential amount of hydrazoic acid formation without sacrificing high yields of 5-phenyl-1*H*-tetrazole.   By introducing only a 10 mol% of a proton source, either TEAHC or TEAPT, in the presence of a stoichiometric amount of quaternary ammonium salt, BTEAC, isolated yields as high as 87 % were achieved.

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CHAPTER III

THE SYNTHESIS AND CHARACTERIZATION OF GLYCIDYL AZIDE POLYMER

Introduction

To facilitate their use as propellants, energetic materials are typically mixed with a binder. A binder is a cross-linked polymer that provides a matrix that binds the explosive ingredients together with a plasticizer. The plasticizer is added to not only facilitate processing, but to improve the mechanical properties of the final formulation. After the curing process, the binder is a rigid and tough elastomeric rubber capable of dissipating and absorbing energy from hazardous stimuli (Provatas, 2000). One of the first binders used in energetic materials was a mixture of nitrocellulose and nitroglycerine. The nitrocellulose thickened the nitroglycerin and reduced the impact and friction sensitivity of the propellant. (Leeming, 1996) Currently, the favored practice is the encapsulation of the explosive in a binder composed of a polymer such as hydroxyl-terminated polybutadiene crosslinked with isocyanates and a plasticizer such as dioctyl adipate. (Provatas, 2000) This system produces a tough, yet flexible, three-dimensional network.

A number of binders—including azide and non-azide species—for use in advanced propellant formulations have been studied (Niehaus, 2000). One of the most popular binders is glycidyl azide polymer (GAP) or poly[(azidomethyl)ethylene oxide] (Figure 3-1). GAP was first synthesized in 1972 by Vandenburg (Vandenburg, 1972). The physical and energetic characteristics of GAP make its use as a binder very important. The low glass transition temperature of GAP and its low percentage of
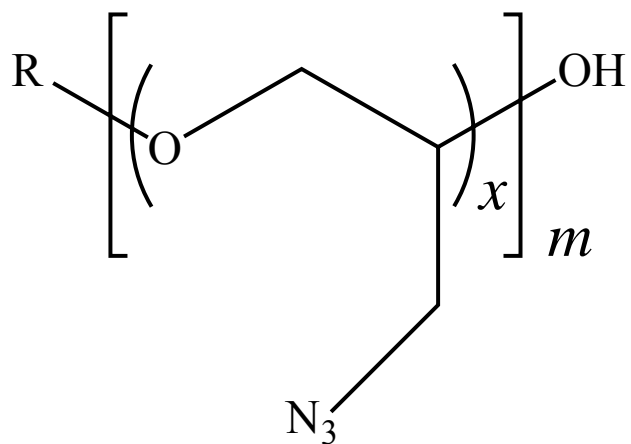
Figure 3-1.   Glycidyl Azide Polymer (GAP) is a viscous amber liquid.

polymer weight-bearing chain make it an energetically favorable substance for use in binder systems (Kim *et al*, 2002; Korobeinichev *et al*, 2002).

In most solid propellants, the polymer content (from the binder) composes only 5-15% of the total propellant formulation. Nonetheless, the polymer ingredient affects the properties of the propellant. Prior to the development of GAP, the polymer component of most binders was the least energetic material in the entire mixture. GAP was designed to overcome this disadvantage by providing energetic properties to every component in the propellant formulation (Frankel, 1979). Based on the density impulse, the energetic properties of GAP were found to be highly competitive with existing propellants (Kuwahara, 2000). The azide groups on GAP are responsible for the energetic characteristics. Each N_3 group has an energy of 80 kcal/mol and adds 2 seconds to the specific impulse (Isp) of metallized propellants and 6 seconds in non-metallized propellants. (Johannssen, 1988) During the combustion of GAP, the azide group undergoes a chain scission to produce nitrogen gas with a heat of reaction of +957 kJ/kg at 5 MPa (Kubota, 1988; Kubota, *et al* 1990). Despite the high energy released by the azide group, researchers have discovered that the safety characteristics of an RDX(Cyclotrimethylenetrinitramine) and GAP mixture (86.4/13.6) has the same safety characteristics as the combination of RDX and the inert binder HTPB(Hydroxyl terminated polybutadiene) (86.4/13.6) (Desai *et al*, 1996).

Currently, only one major manufacturer in the United States produces GAP. The specifications and properties of the available material are very limited as only one molecular weight, PDI, and functionality are produced. The molecular weight and functionality of GAP are very important with regard to achieving the desired level of

cross-linking of the cured propellant mixture (Ampleman, 1990). The goal of this research was to synthesize several GAP materials with various specifications. These experiments were designed in an attempt to control the molecular weight, functionality, and polydispersity of GAP. As always, process improvement was another guiding principle during this research.

<center>Experimental Methods</center>

Materials

The chemicals used in these experiments were purchased and used without additional purification. The chemicals used included: epichlorohydrin (Aldrich, 99.9%), stannic chloride (Aldrich, 99.9%), 1,4-butanediol (Aldrich 99%), 1,3-propanediol (Aldrich, 99.98%), trifluoroacetic acid (Aldrich, 99%), sodium azide (Aldrich, 99.98%), Aliquat 336 (Aldrich, 99%), dichloroethane (Aldrich 99.9%), [BMIM][PF$_6$] (Alrich, 99%), [BMIM][BF$_4$] (Aldrich, 99%), dimethylsulfoxide (Aldrich, 99%)

Procedure

All of these reactions were run with an overhead stirrer. Unless noted otherwise, the stir rate was 180 RPM. Three- or four-necked flasks were used in all of these procedures. To measure the molecular weights and polydispersities of the polymers, a GPC was used that had been calibrated using the low molecular weight range polystyrene Easy-Cal strips. Structural analysis was performed using IR spectroscopy, ^{13}C, and ^{1}H NMR and the data corresponded to the analysis found in the literature. All of the

<center>43</center>

reactions involving GAP were performed on a small scale (3.0g or less) and encased behind a blast shield.

(Figure 3-2) Synthesis of PECH. 1,4-butanediol (1.076 mL, 0.0121 mol) was added to a four-necked roundbottom flask. 1,2-dichloroethane (4.00 mL) was then added and allowed to stir for several minutes. Nitrogen gas was then run through the system. While stirring, trifluoroacetic acid (0.116 mL, 1.51 mmol) and stannic chloride (0.04 mL, 0.342 mmol) were added via syringe. The contents were then lowered into an ice bath and epichlorohydrin (20.0 mL, 0.255 mol) was slowly dripped into the solution. After the addition of epichlorohydrin was complete, the solution was heated to 65° C for one hour. 10% aqueous methanol with 0.25 mL of NaEDTA was then used to wash the reaction. The wash was repeated without the NaEDTA 3 more times before the organic phase was dried with $MgSO_4$ and placed in the drying oven to remove the dichloroethane. Isolated yields of 96% were obtained. PECH: ^1H, δ (d-$CDCl_3$): 3.55-3.78 (m, 2H, 2H, H); ^{13}C, δ (d-$CDCl_3$): 26.58 (CH_2), 43.89 (CH_2), 69.84 (CH), 79.29 (CH_2). IR displayed stretching at 3450 cm^{-1} (-OH), 1120 cm^{-1} (C-O-C), 748 cm^{-1} (C-Cl).

(Synthesis of Catalyst Mixture) Stannic chloride (10.08g, 38.24mmol), trifluoroacetic acid (20.88g, 0.180mol), and 1,2-dichloroethane (48mL) were added to a dried 100mL round bottom flask. The solution was stirred vigorously with a magnetic stirrer for 20 minutes. The flask was capped with an air-tight rubber stopper and stored at 5°C.

(Figure 3-4) Polyepichlorohydrin (3.0g, 30.0mmol) was weighed into the flask followed by the addition of Aliquat 336 (0.455g, 1.12 mmol). The flask was then secured in the hood and DMSO (5mL) was added. The mixture was stirred and sodium azide (2.217g, 34mmol) was added. More DMSO (5mL) was added and the reaction was heated to 80°C for 24 hours. The reaction was then cooled down with the aid of an ice bath and washed with water. The water was then decanted and the rinse was repeated 3 times. The flask was then placed in a vacuum oven overnight at 50°C. Process resulted in complete conversion of the PECH. GAP: ^{1}H, δ (d-CDCl$_3$): 3.26-3.95 (m, 2H, 2H, H); ^{13}C, δ (d-DMSO): 29.37 (CH$_2$), 51.71 (CH$_2$), 60.72 (CH$_2$), 69.57 (CH), 78.72 (CH$_2$). IR revealed pattern stretching at 2100 cm^{-1} (C-N$_3$) and 1075 cm^{-1} (C-O-C).

(Figure 3-7) Polyepichlorohydrin (2.30g, 23 mmol) was added to a 3-necked round bottom flask. 1-butyl-3-methylimidazolium hexafluorophosphate (3.0 mL), or 1-butyl-3-methylimidazolium tetrafluoroborate (3.0mL) was then added to the flask. Stirring was commenced and sodium azide (1.8106g, 27 mmol) was added. The reaction was heated to 100°C for 48 hours. Upon completion, water and diethyl ether were added to the reaction. The two phases were then separated and the aqueous phase was washed with ether. The oranic phase was washed with water three times. The organic phases were then combined and dried with MgSO$_4$. After the solvent was reduced via rotary evaporator, the product was placed in a vacuum oven overnight at 50°C.

<u>Results and Discussion</u>

The first step in the synthesis of GAP is the polymerization of epichlorohydrin (ECH). This procedure is an exothermic epoxide ring-opening polymerization of which there are many examples in the literature (Frankel, 1992).

The general descriptions of reactant stoichiometry and reaction conditions for the initial experiments are shown in Figure 3-2. In this reaction, butanediol reacts with the epichlorohydrin to initiate the polymerization. The $SnCl_4$ complexes with the oxygen on the monomer to facilitate this process. A depiction of this mechanism is shown in Figure 3-3. The stannic chloride was a necessary ingredient, as the reaction did not occur without it. Several experiments were attempted without trifluoroacetic acid (TFA). While the experiments without TFA produced some product, the process was much more efficient when the TFA was present. The TFA and the stannic chloride reacted to form the triflate seen in Figure 3-3. The addition of this group to the stannic chloride further depleted the electron density of the tin center. This led to a stronger coordination with the oxygen of the epichlorohydrin, which was essential for the successful activation of the monomer.

Altering the number of hydroxyls on the diol initiator provided the ability to change the functionality of the polymer, and did not alter the overall result of the reaction. In these experiments, butanediol, propanediol, and 1,2,3-propanetriol were all used with success. While altering the number of hydroxyls on the diol did not affect the outcome of the reaction, the properties of the product changed. Aside from a higher functionality, the tri-functional PECH had a higher viscosity and darker color.

Reaction scheme:

ECH
(20mL)

+

$HO(CH_2)_4OH$

~5 mol %
(rel. to ECH)

65°C, 1 Hour
$ClCH_2CH_2Cl$
(5mL)

$SnCl_4$ / TFA
~0.2 mol%
(rel. to ECH)
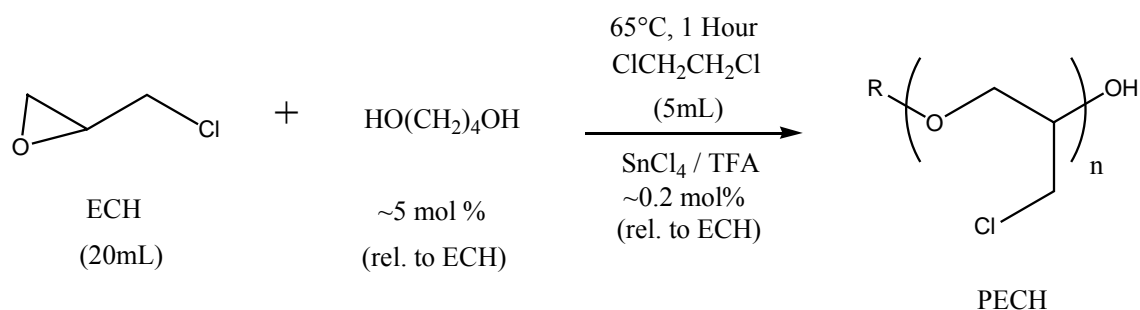
PECH

Figure 3-2.   The general process for synthesizing PECH. In this depiction, 1,4-butanediol is the initiator, however, the reaction is also successful with 1,3-propanediol and 1,2,3-propanediol.
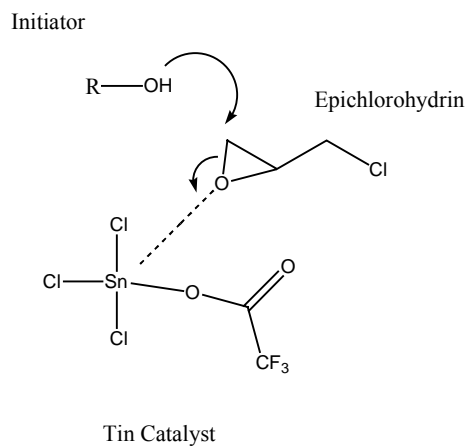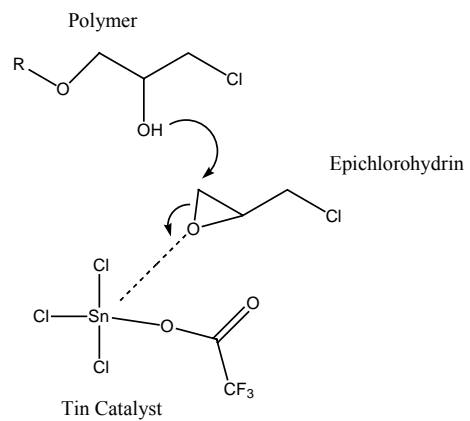
Figure 3-3.   The general mechanism for the polymerization of epichlorohydrin.

In the test used to control the molecular weight of the polymers, butanediol was used as the initiator. To serve as an effective binder, a molecular weight of roughly 2000 is required for GAP. This weight gives the polymer a viscosity comparable to other binders currently used in rocket motors. To achieve this molecular weight, an experiment was run with 0.0121 mol of butanediol and 0.255 mol epichlorohydrin and 0.2 mol% of the catalyst relative to ECH. Calculations revealed that if the reaction approached completion with this monomer:initiator ratio, a polymer with a molecular weight of 2000 would be obtained. However, the experimental molecular weight for this polymer was ~3300 (PDI = 1.1). The experiment was repeated and once again a molecular weight near 3000 was obtained.

It was believed that this high molecular weight was caused by an inadequate activation of the monomer. To ensure that all of the hydroxyl groups on the butanediol reacted, it was suggested that more catalyst should be used. However, safety concerns about this reaction removed this course of action from consideration. The epoxide ring opening is an exothermic process. During several of the initial experiments, starting material was ejected from the condenser when the reaction started. Given the extreme toxicity of epichlorohydrin and stannic chloride, this occurrence created a potentially dangerous situation. Since the addition of more catalyst would have increased this risk, a different approach was taken.

One of the concerns throughout the beginning of this project was the volatility of the stannic chloride. This problem was magnified by the flow of nitrogen gas through the system. Another concern was the mixing of the trifluoroacetic acid and stannic chloride in the dichloroethane. Due to the volatility, the addition of epichlorohydrin was started as

soon as the catalyst and TFA was added. This immediate addition may not have allowed the triflate to form before the addition of the monomer. To address these issues, a pre-mixed catalyst solution was prepared. The catalyst cocktail included stannic chloride, TFA, and dichlorethane. This technique ensured that none of the volatile catalyst would be lost during the addition. Also, the pre-mixing allowed plenty of time for the triflate to form prior to its introduction into the reaction flask.

The general procedure with butanediol was then repeated using the catalyst cocktail. The molecular weight of the polymer from this process was ~1600. This result was much closer to the desired weight of 2000 and proved that the problems with the catalyst were assuaged by the use of the cocktail.

A series of reactions were also run in an attempt to vary the polydispersity (PDI) of the polymers in situ. These efforts included adding the monomer in delayed phases and alternating the addition of monomer and initiator. Unfortunately, these efforts were unsuccessful, as the PDI never strayed from the 1.1-1.3 range. Despite this disappointment, PECH starting material was synthesized so that GAP could be produced.

The first experiments run to produce GAP involved the use of a simple phase transfer catalyst. In this case, the phase transfer catalyst was a quaternary ammonium salt that formed a reactive species with sodium azide. This reactive species transferred the azide into the organic phase to react with the dissolved polymer (Starks, C. M. et al, 1994). The general reactant stoichiometries and reaction conditions can be seen in Figure 3-4. In this process, the sodium azide formed a reactive species with the Aliquat 336 (US 4,268,450). The azide then replaced the chloride on the side chain of the PECH. In only 24 hours at 80°C, the process completely converted the bi- and tri-functional PECHs into
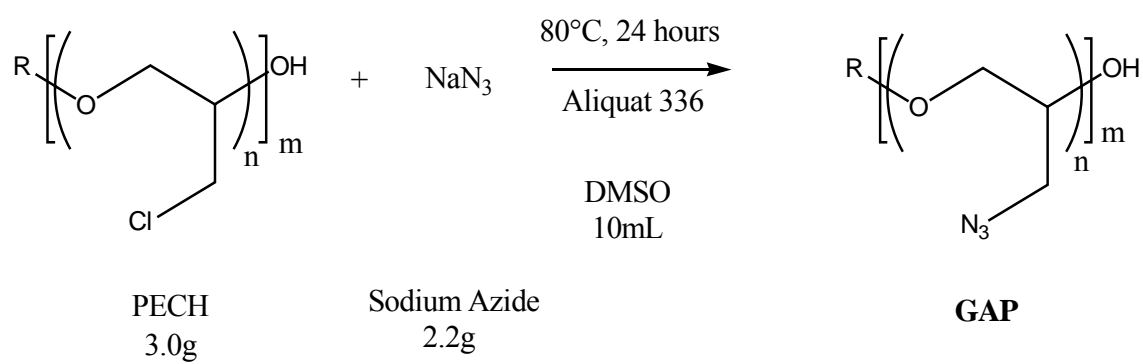
Figure 3-4.   The general GAP reaction.

GAP (Figure 3-5). This process produced GAP with a higher functionality when the trifunctional PECH was used. Raising the functionality by using the tri-functional starting material was much simpler than other techniques that employed regioselective epoxidation of linear PECH in basic conditions (US 5,256,804).

For all of these reactions, strict safety measures were followed. Teflon coated spatulas were used, and blast shields encased all of the reactions because GAP is an explosive compound. In addition to performing the reactions on a very small scale, the GAP in solution was never heated beyond 80°C. The pure products were not exposed to temperatures over 50°C. These guidelines were adopted from the safety protocols at ATK Thiokol. The only drawback to this process was the use of DMSO. While it served the reaction well, the removal of this solvent was very difficult. Safety was also a concern with DMSO. Like sodium azide (which is extremely toxic), DMSO is readily absorbed through the skin. In combination these chemicals have to be handled with extreme care. However, the use of DMSO was considered safer than the methods that employ aqueous solvents due to the possibility of forming hydrazoic acid (US 4,379,894). Due to these concerns, it was decided that ionic liquids should be employed to aid in the synthesis of GAP.

Ionic liquids are quite simply molten salts that are liquids at room temperature and standard pressure. They consist of an anion and a cation and have no measurable vapor pressure. For the purposes of making GAP it was believed that the ionic liquid could serve not only as a solvent but as a replacement for Aliquat 336. The use of the ionic liquid ensured the presence of a large excess of a quaternary salt that would likely speed up the reaction.

Figure 3-5.   Two samples of GAP. The sample on the left is bi-functional GAP
               synthesized with 1,4-butanediol. The sample on the right is tri-functional
               GAP synthesized with 1,2,3-propanetriol.

Two ionic liquids were tested. They were 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF$_4$]) and 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF$_6$]). These liquids are pictured in Figure 3-6. The key difference between these ionic liquids is their hydrophilicity. The [BMIM][BF$_4$] is hydrophilic because of its polar nature. The [BF$_4$] anion creates this high polarity because it is a small anion with a concentrated negative charge. The [BMIM][PF$_6$] is hydrophobic because the larger size of the anion disperses the charge over a larger area. This dispersion dimishes the polarity of the molecule. The cation can also be tuned to inhibit or promote hydrophilicity by adjusting the length of the alkyl chains. This feature will be very important in Chapter VI.

Unfortunately, the processes that employed ionic liquids were unsuccessful. The general reactant stoichiometries and reaction conditions are shown in Figure 3-7. Initially, it was postulated that the hydrophobic ionic liquid would work best due to the sensitive nature of sodium azide. However, after 48 hours at 100°C [BMIM][PF$_6$] did not produce any GAP. When [BMIM][BF$_4$] was used, however, these same conditions converted 20% of the sidechains to GAP. The process was repeated at 50°C and 80°C and yields of 0 and 8% respectively were achieved. The reasons for these low yields were unclear. The reaction might have been mass transfer limited by the viscosity of the ionic liquid. A co-solvent would possibly ameliorate this problem. Such an addition might also assist in the ion exchange between the salt and the sodium azide.
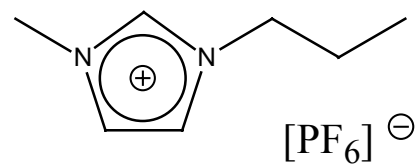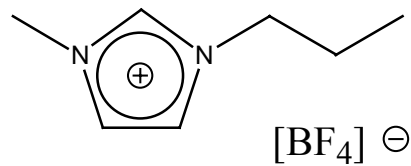
[BMIM][BF$_4$]   [BMIM][PF$_6$]

Figure 3-6.   Two generalized structures of common ionic liquids.
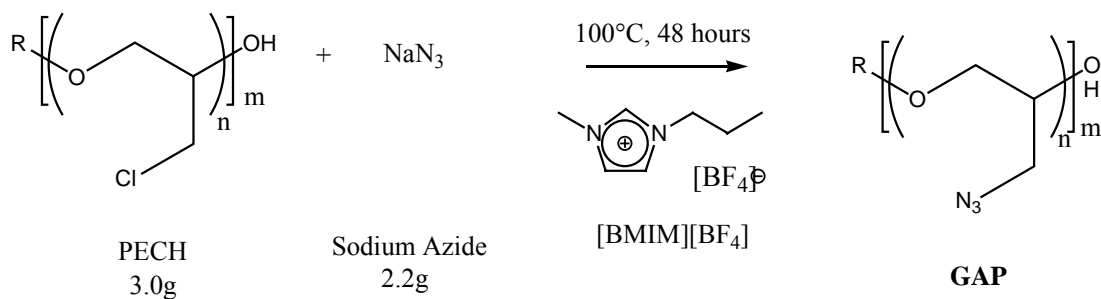
Figure 3-7.   This procedure is the process for producing GAP in ionic liquids. This
              depiction shows [BMIM][BF4], however, [BMIM][PF6] was also tested.

<u>Conclusion</u>

The procedures in this chapter successfully produced PECH and GAP with the desired properties. Although the hydroxyl-terminated polymers were used throughout this thesis, the GAP polymers can be further functionalized (EP, 0-296-310). These possibilities expand the possible uses of GAP in energetic materials.

Aside from the ability to produce GAP with the desired molecular weight and functionality, the main lesson learned from these experiments was the safe handling of GAP. Explosive materials were used in each of the remaining chapters of this thesis. The work in this chapter laid the groundwork for the safety procedures that were followed throughout the rest of this work. By following the procedures in this chapter, GAP can be safely and efficiently produced.

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CHAPTER IV

THE SYNTHESIS AND CHARACTERIZATION OF
GLYCIDYL TETRAZOLE POLYMERS

Introduction

In Chapter III, glycidyl azide polymers (Figure 4-1) were prepared by substituting the chlorine on the sidechain of polepichlorohydrin with an azide moiety. While the presence of the azido group adds the desired energy to GAP, it leads to other significant problems. The first problem occurs during the curing process. GAP is usually cured with aliphatic isocyanates. This process creates urethane linkages with the hydroxyl end groups of the GAP. The isocyanates are also capable of reacting with the azido groups present in the GAP (Kasikci, 2000; Panda, 2000). A fast cure process that rapidly depletes the isocyanate groups has been employed to attempt to overcome this problem. These fast cures lead to short propellant pot-lives which makes propellant processing and motor casting more difficult. Additionally, the cure catalysts often contain metal ions which are known to decompose organic azides (Balteanu, 2004). The "pot-life" of a propellant mixture is a measure of how long a propellant mixture can be manipulated before it hardens or cures. A short pot-life means that there is little time to cast the propellent into a mold. A longer pot-life simply means that the propellant formuation takes longer to harden or cure.

Also, the general reactivity of the azido groups leads to other problems. Upon storage, degradative processes introduce double bonds in the binder's structure. These double bonds have the potential to react with the azido group to form unstable triazole intermediates. These species react to release N_2. Nitrogen gas is insoluble in the
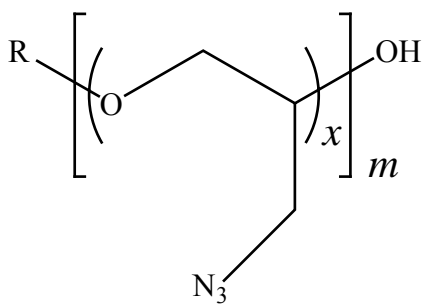
Figure 4-1.   Glycidyl Azide Polymer (GAP) is a viscous amber liquid.

binder and will result in voids in the cured propellant (Frankel, 1985). In terms of processibility, safety, toxicity, and storability, GAP is not an ideal energetic material.

The goal of this research was to preserve the energetic advantages provided by GAP while ameliorating the drawbacks caused by the reactivity of the azido group. To accomplish this goal the research focused on replacing the $-N_3$ with the more stable tetrazole moiety. The results of this research produced a glycidyl tetrazole polymer (GTP) (Figure 4-2). The tetrazole was chosen for its stability and energetic properties. In a heat of formation comparison calculation using Spartan (See Chapter VI), the CH_2N_3 side chain and the tetrazole ring ($-CHN_4$) had ΔH_f of 313.8 and 280.1 kJ/mol respectively. In another calculation the energetic impulse of GAP and GTP was compared. Once again, they displayed similar results as GAP and GTP measured 272.4 and 250.0 respectively. Based on these calculations, it was decided that the replacement of the azide with the tetrazole ring would preserve the energetic properties of the polymer. It was believed that the tetrazole moiety would be a stable, non-reactive—yet energetic—species that would provide a preferred alternative to the troublesome azido group.

<u>Experimental Methods</u>

<u>Materials</u>

The chemicals used during this investigation were obtained and used without further purification. The chemicals used included the following: polyepichlorohydrin (See Chapter III), glycidyl azide polymer (See Chapter III), dibutyltin dilaurate (Aldrich, 95%), dichloroethane (Aldrich, 99+%), sodium azide (Aldrich, 99.99+%), Aliquat 336,
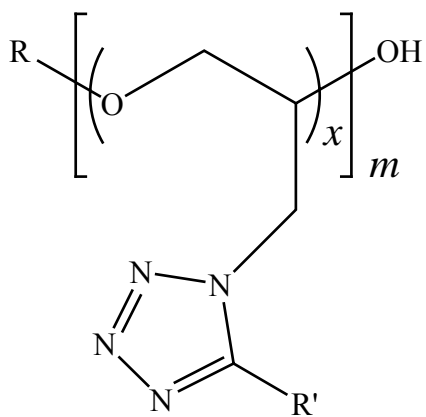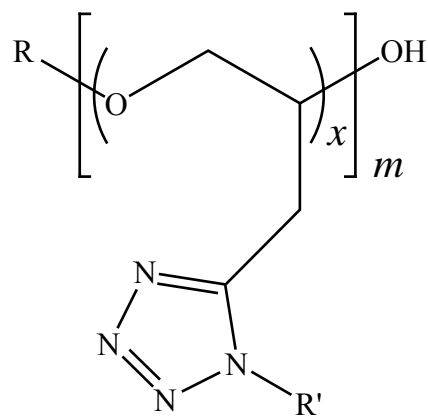
Figure 4-2.   Glycidyl Tetrazole Polymers (GTP). .

dimethyl sulfoxide (Aldrich, 99+%), toluene (Aldrich, 99.8%), p-toluenesulfonyl cyanide (Aldrich, 95%), ethyl cyanoformate (Aldrich, 99%), benzyl cyanoformate (Aldrich, 97%), lithium hydroxide (Aldrich, 98+%), tetrahydrafuran (Aldrich, 99.5+%), methylene chloride (Aldrich, 99+%), hydrochloric acid (Aldrich, 37%), and ethyl acetate (Aldrich, 99.8%).

Procedure

All of the reactions described below were performed in a 100 mL (14/20) 3-neck round bottom flask. In each experiment, an overhead mechanical stirrer was used to facilitate adequate mixing of the polymers. Unless otherwise noted, the standard stir rate was 150 RPM. A water-cooled condenser was also used in each experiment. The remaining neck was used to add solid reactants to the system. During the reactions, a rubber stopper was used to seal the outlet. Heating mantles and temperature controllers were also used in all of these experiments. Whenever a volatile solvent was involved, a water flow safety monitor was attached to the condenser. In all of these tests, the polymer was the limiting reagent; therefore, all of the mol percent values are relative to the starting material polymer.

(Figure 4-3) Polyepichlorohydrin (PECH) (5.00g, 54 mmol) was first weighed into the reaction flask. This step was followed by the addition of 10 mol % of Aliquat 336 (2.18g, 5.4 mmol) or tetrabutylammonium bromide (TBAB) (2.08g, 5.4 mmol). The flask was then clamped in the hood and toluene (15mL) was added. The water-cooled condenser was then attached and stirring was commenced. 1.2 equivalents of NaCN (3.17g, 65 mmol) was then added followed by toluene (15mL). The mixture was heated

for 72 hours at 60°C. Upon completion, water (15mL X 3) was used to wash the toluene phase. The toluene was then evaporated with the aid of a rotary evaporator. The polymer was placed in the drying over overnight.

(Figure 4-4) Glycidyl azide polymer (GAP) (1.0g, 10 mmol) was weighed into the reaction flask and clamped into the fume hood. Toluene (2mL) was then added and stirring was started. p-Toluenesulfonyl cyanide (2.00g, 11 mmol) was then added followed by toluene (2mL). The mixture was heated to 80°C and stirred for 72 hours. The product was rinsed with toluene (10mL). The solvent was decanted and the product was placed in the vacuum oven to remove the residual solvent. Quantitative yields were obtained. ^{13}C, δ (d-DMSO): 22.11 (CH$_3$), 29.41 (CH$_2$), 51.55 (CH$_2$), 60.42 (CH$_2$), 69.51 (CH), 78.79 (CH$_2$), 129.81 (CH), 130.46 (CH), 136.63 (C), 147.94 (C), 155.42 (C)

(Figure 4-8) Glycidyl azide polymer (GAP) (0.5g, 5 mmol) was weighed out into the reaction flasked and secured in fume hood. Stirring was commenced. Ethyl cyanoformate (3.0g, 30 mmol) or benzyl cyanoformate (4.0g, 25 mmol) was then added to the flask. The mixture was then heated to 100°C or 50°C and reacted for 168 or 72 hours respectively to obtain 100% conversion. Upon completion, water (3mL) was added to the reaction followed by ethyl acetate (15mL). Saturated sodium bicarbonate (20mL) was then added and stirred for 1 hour. The organic layer was separated, washed with MgSO$_4$, reduced via rotary evaporator, and placed in a drying oven overnight (50°C). Ethyl-GTP -^{13}C, δ (d-DMSO): 22.74 (CH$_3$), 29.47 (CH$_2$), 50.89 (CH$_2$), 60.42 (CH$_2$), 63.64 (CH$_2$), 69.85 (CH), 79.12 (CH$_2$), 147.25 (C), 152.60 (C). Benzyl-GTP-^{13}C, δ (d-

DMSO): 29.37 (CH$_2$), 51.71 (CH$_2$), 60.06 (CH$_2$), 66.96 (CH$_2$), 69.73 (CH), 79.20 (CH$_2$),

128.63 (CH), 129.07 (CH), 129.18 (CH), 136.13 (C), 143.22 (C), 155.12 (C)

Ethyl-GTP (0.30g, 1.50 mmol) or benzyl-GTP (0.50g, 2.0 mmol) was weighed

out into the reaction flask and secured in the fume hood. Tetrahydrafuran (3mL) was

then added to the reaction and stirring was begun. 1M HCl (2mL, 2.0 mmol) was added

dropwise to the solution. The reaction was then heated t 50°C and stirred overnight. The

reaction was cooled on ice. Tetrahydrafuran (20mL) and water (20mL) were then added.

The mixture was transferred to a separatory funnel and washed with saturated sodium

bicarbonate (20mL). The organic phase was washed with water (20mL X 3) and dried

with MgSO4. The organic layer was then reduced via rotary evaporator and placed in a

vacuum oven overnight.

(Figure 4-9) Ethyl-GTP (0.5g, 2.3 mmol) or Benzyl-GTP (0.70g, 2.6 mmol) was

added to the reaction flask and secured in the fume hood. Tetrahydrafuran (4mL) was

then added and stirring was started. 3 equivalents of LiOH (0.167g, 6.9 mmol) were then

added to the solution. A solution of LiOH and water was used for this purpose (0.25g

LiOH/10 mL water). The reaction was heated to 50°C and stirred for 24 hours. Upon

completion, water (20mL) and ethyl acetate (20mL) were added to the cooled reaction.

After 10 minutes of stirring, HCl (10%) was added dropwise until the solution was acidic

(pH ~ 2). The organic layer was then separated, washed with MgSO4, reduced via rotary

evaporator, and placed in a vacuum oven overnight (50°C). ^{13}C, δ (d-DMSO): 29.41

(CH$_2$), 48.19 (CH$_2$), 60.42 (CH$_2$), 68.75 (CH), 77.08 (CH$_2$), 145.39 (C).

The goal of this research was successfully accomplished by replacing the azide group on the side chains of GAP with a tetrazole. The initial strategy involved replacing the –Cl on the side-chain of PECH with a –CN group. There were two reasons why this strategy was selected. The first was that the –CN on the sidechain could be easily converted into a tetrazole through the cycloaddition of sodium azide (Benson, 1967; Butler, 1977; Herbst, 1957; Koguro, 1998; Russell, 1993). Second, this technique would not require the explicit use of GAP as a starting material.

Upon searching the literature, a technique was found that converted –CH$_2$Cl side-chains to –CH$_2$CN side-chains (Jean, 1979). The technique was a direct substitution of the chlorine with the nitrile. The procedure was followed explicitly and repeated several times. Unfortunately, the reaction failed to produce any cyano substituted polymer. This technique was subsequently abandoned and phase transfer catalysis (PTC) was employed.

PTC was used in an effort to introduce the NaCN salt into the organic phase that dissolved the polymer. The technique used closely mirrored those found in the literature (Dozeman, 1997; Starks, 1994). This process (Figure 4-3) was attempted using two phase transfer catalysts: Aliquat 336 and tetrabutylammonium bromide. Despite repeated attempts, the procedure failed to produce any cyano-substituted polymer. Although the reasons for this failure were unclear, it was believed that the process may have formed carbenes along the polymer side-chains. This theory was devised based on the bright orange colors observed during the first few hours of the reactions. The cyano group likely acted as a base and deprotonated the alpha hydrogens along the side chain.
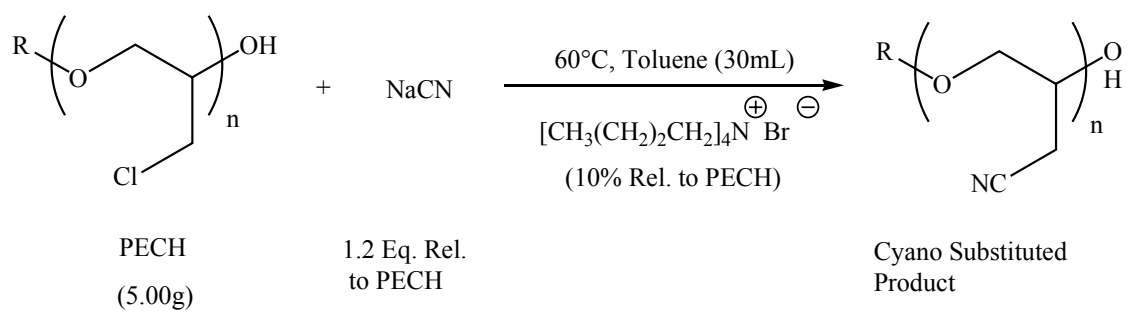
Figure 4-3. Phase transfer catalysis process designed to replace the chlorine of polyepichlorohydrin with a cyano group.

These carbenes could have easily reacted with other nitrile groups attached to the polymer. Another possible reason for this failure was the viscous nature of the polymer. The benefits of PTC may not have overcome the limitations placed on mixing by the polymer's viscosity.

At this point, it was decided to attempt the synthesis using GAP as the starting material. While this decision heightened concerns about safety, all of the reactions never utilized more than 1.0g of GAP. In a recently reported method, researchers used "click-chemistry" to produce tetrazoles from organic azides (Demko, 2001). By adding a cyanide with an electron withdrawing group to a series of organic azides, the researchers produced tetrazoles with 100% conversion. In addition to these results, the work-up involved was very simplistic. In the reactions that used small molecules as starting materials, the only workup required was the removal of the product from the Teflon coated stir bar. Therefore, a number of experiments were run using GAP as the organic azide and p-toluenesulfonyl cyanide as the cyano group (Figure 4-4). Although GAP is a liquid at room temperature, the reaction was run with a co-solvent due to its high viscosity. To assist in the mixing of the reactants, a small amount of toluene was introduced into the system. On every front, this reaction was a success.

The pure tosyl-GTP product was an orange solid. While this was expected, this physical characteristic would disqualify tosyl-GTP from serving as an energetic binder. Therefore, a series of GAP/tosyl-GTP polymers were synthesized. The picture in Figure 4-5 depicts the transformation from the liquid GAP to the solid tosyl-GTP. As the picture indicates, the polymer remained a liquid until more than 60% of the $-N_3$ groups were replaced with tetrazoles. This opened up the possibility that a hybrid compound could be
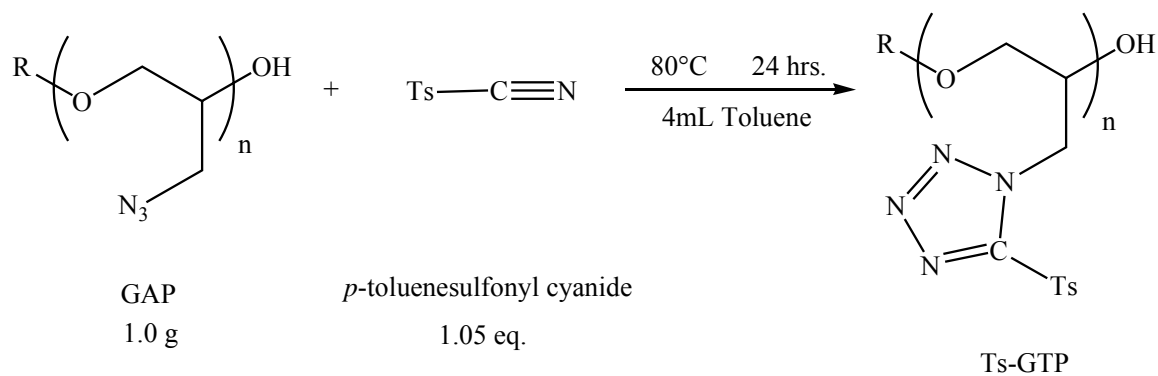
Figure 4-4.   The Sharpless "click" process to produce the tosyl-substituted glycidyl azide polymer.
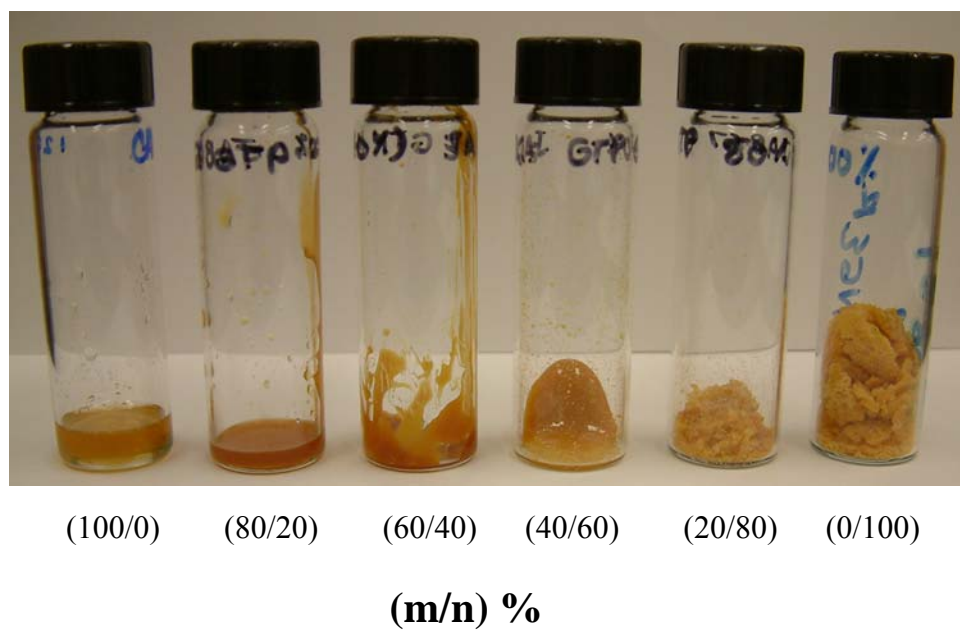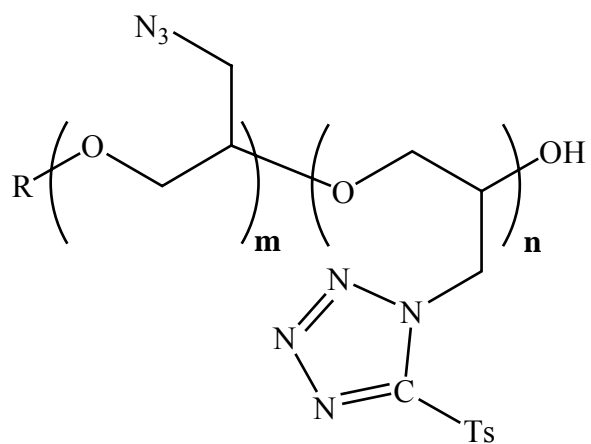
Figure 4-5.   The physical properties of a wide range of GAP/Ts-GTP compounds.

used as a propellant. Energetic tests were then conducted on these polymers using differential scanning calorimetry (DSC). The DSC data was collected (Figure 4-6) and the extent of the exotherms were evaluated via peak integration (Figure 4-7). The polymers that had a higher GAP content also had a stronger exotherm. It was believed that the size and stablilty of the tosyl group adversely affected the energetic properties of the molecule.

Accordingly, the work refocused on producing a hydrogen substituted GTP polymer as shown in Figure 4-2 (R' = H). It has been shown that a number of cyanoformates will react with organic azides (Demko, 2001). It was proposed that if the product from this reaction was followed with a successful decarboxylation, the hydrogen substituted GTP derivative could be easily obtained. Once again, GAP would be the starting material, but very small amounts were used due to safety concerns. For the purpose of these experiments, ethyl and benzyl cyanoformate were used. In both cases, the process was a success (Figure 4-8). However, the ethyl cyanoformate derivative required 7 full days to go to completion. Benzyl cyanoformate offered a small improvement, but still required a full 3 days to reach completion. The ethylester-GTP was a solid at room temperature, whereas the benzylester-GTP was a liquid.

At first, an acid catalyzed decarboxylation was attempted on both derivatives. Unfortunately, these efforts were unsuccessful. A base-catalyzed process using LiOH however, provided the necessary conditions for decarboxylation (Figure 4-9). While both derivatives successfully decarboxylated using this technique, the benzyl-GTP derivative created a problem. In the ^{13}C NMR, benzyl alcohol (bp=210°C) continually appeared.
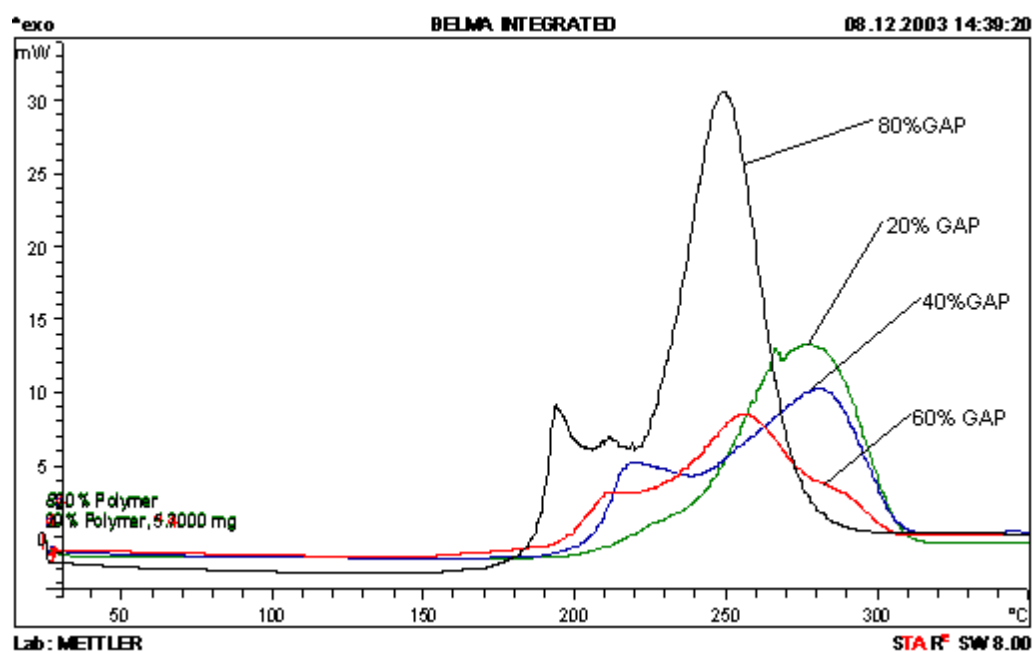
Figure 4-6.   Differential scanning calorimetry data for the GAP/Ts-GTP polymer.

Tosyl-Glycidyl Tetrazole Polymer Energy
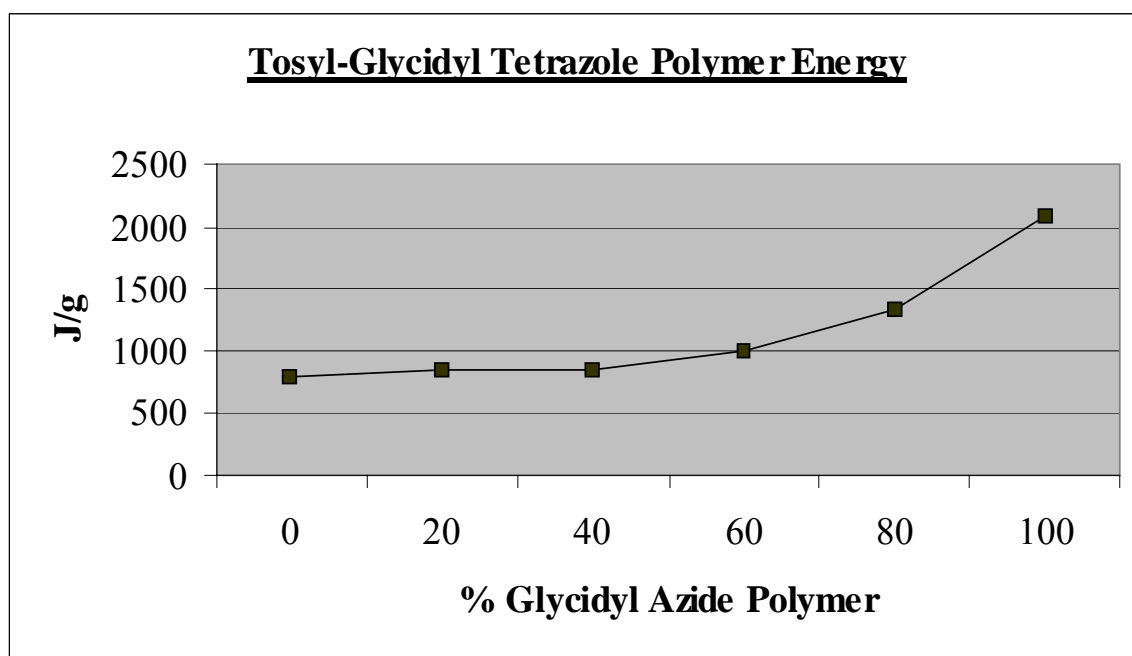
Figure 4-7.   Exotherms observed for Ts-GTP as the GAP component was replaced with the tosylated tetrazole moiety
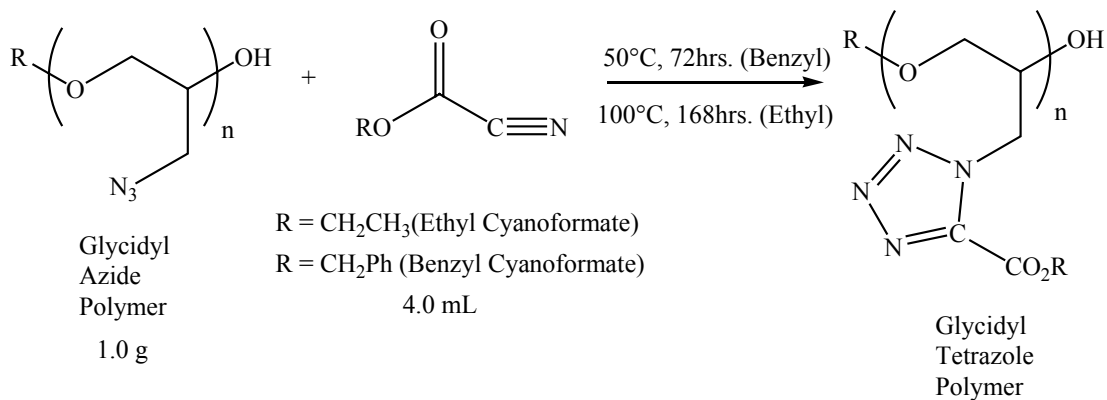
Figure 4-8.   Reaction conditions for the addition of the cyanoformates to GAP.
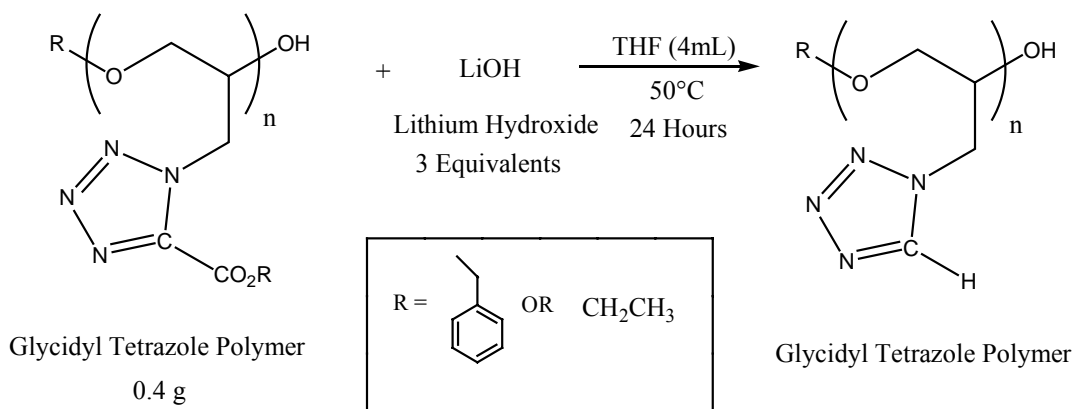
Figure 4-9.   Decarboxylation of the esters to produce the H-substituted glycidyl
tetrazole polymer.

While this indicated a successful cleavage of the ester, it illustrated the difficulty of removing this by-product without a laborious workup. The ethyl derivative was therefore the preferred starting material because ethanol was easily removed during the standard workup. The final product, GTP (Figure 4-2A), was a solid.

Finally, a comparison of the DSC data for every derivative was plotted. While the substituted GTP derivatives all exhibited exotherms that were less than half of GAP's, the hydrogen substituted GTP produced an exotherm equal to 75% of GAP. All of this data is presented in Figure 4-10 and Table 4-1. Clearly, this data proves that the R' group from Figure 4-2 played a key role in the exotherm strength for each of the derivatives.

Conclusion

The results of this research proved that a wide variety of tetrazole substituted GAP polymers could be synthesized. While the exotherms for the H-GTP derivative (Figure 4-2A) were not as large as the GAP exotherm, the benefits with regard to processing and storage might overcome this energetic disadvantage.

Another issue to consider is the difference between the isomers in Figure 4-2. While this research successfully analyzed the exotherm of Figure 4-2A, the exotherm of 4-2B is still unknown. Further testing might show that this alternate isomer has an energetic potential closer to GAP.

Regardless of which isomer is produced, this research clearly illustrated that the R'group from Figure 4-2 played a significant role in determining the size and strength of the exotherm. This group also affected the physical properties of the polymer. This point

Table 4-1.   This table shows the exotherm values of each of the GTP derivatives.
              The colors in the last column correspond to the colors in the DSC data.

Molecule	Energy (J/g)	Energy (kJ/mol)	Color
Glycidyl Azide Polymer	2097	207	Black
H-Glydidyl Tetrazole Polymer	1429	180	Purple
Tosyl-Glycidyl Tetrazole Pol.	797	223	Blue
Ethylester-Glycidyl Tet. Pol.	584	115	Red
Benzyl-Glycidyl Tetrazole Pol.	342	88	Green
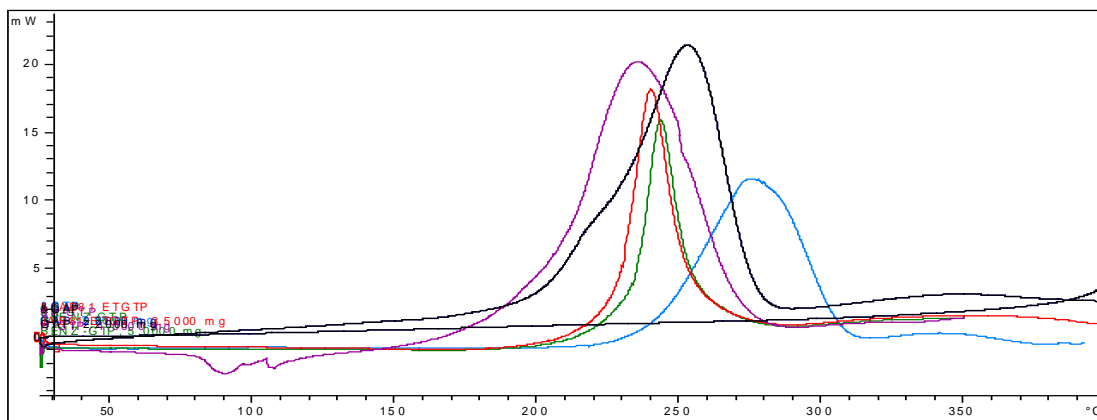
Figure 4-10.   The collection DSC scans for all of the GTP derivatives. The colors
                correspond to the data found in Table 3-1.

was proven by the fact that the ethylester-GTP was a solid at room temperature and the benzylester-GTP was a solid. The exotherms of these two molecules also vastly differed. This data offers conclusive proof that variations on the R' group can significantly impact the overall properties of this polymer. One very interesting possibility would be the placement of an energetic substituent in the R' position. This could be achieved with a substitution on the tosyl-GTP derivative. Such a reaction would allow for both the energetic and physical properties to be altered in a single process.

Another consideration in this project is the molecular weight of the polymers. All of the polymers used in these experiments had a molecular weight around 2000 g/mol. This characteristic could easily be altered during the synthesis of the PECH starting material. Altering this property would provide another opportunity to control the physical properties of the polymer. In addition, using branched starting materials might also assist in this endeavor.

Overall, this project proved that the GTP polymers show potential as a possible replacement for GAP. Even if every tetrazole derivative proved to be a solid, a hybrid polymer could still be produced that would range from a solid to a liquid. An illustration of this concept is shown in Figure 4-5. Such a hybrid would have much fewer $-N_3$ groups than GAP, and would significantly improve the problems that the azido groups cause for this molecule.

It should be noted, however, that the solid GTP could have other applications. Tetrazoles have been discussed as potential air bag propellants. A role such as this could be filled by a solid GTP polymer.

The synthesis of GTP illustrated herein opens up a number of possibilities. The GTP is an energetic polymer with tunable energetic and physical characteristics that shows potential as a GAP replacement.

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CHAPTER V

THE SYNTHESIS AND CHARACTERIZATION OF ENERGETIC FOAMS

Introduction

In the previous chapters, the synthesis of nitrogen-rich energetic polymers was discussed. The glycidyl azide polymers (GAP) and the glycidyl tetrazole polymers (GTP) have hydroxyl-terminated chains. It is well known that through urethane chemistry hydroxyl-terminated polymers can be transformed into foams. Since their invention by Bayer in 1937, polyurethanes have become the most well known polymers used to make foams. They are also the most versatile family of polymers. They are used to make elastomers, fibers, and adhesives (Wilson, 1989). In this project, urethane linkages were formed with the end groups of the energetic polymers (Figure 5-1). Gas bubbles were then introduced to generate an energetic foam.

An energetic foam would have a number of possible applications. For most propellants, a binder is used to give the propellant a solid support structure that fills rocket motors. For liquid propellants it is conceivable that an energetic foam could be used to absorb the substance before it is placed in a motor. Any foam could be used for this purpose, however, an energetic foam would contribute to the overall energy of the system. In the past, foamed propellants have been widely studied (Messmer, *et al* 2001; Bohnlein-Maub, 2002), but the foaming of the binder itself has received limited attention (Sanderson, 2000). A foamed propellant is less applicable, because of the low density of foams. This lowered density would be an advantage in a binder, however, because the empty spaces could be filled with propellant.

A Urethane

GAP/GTP   Diisocyanate   Energetic Foam
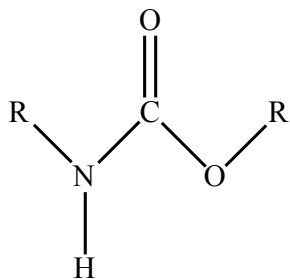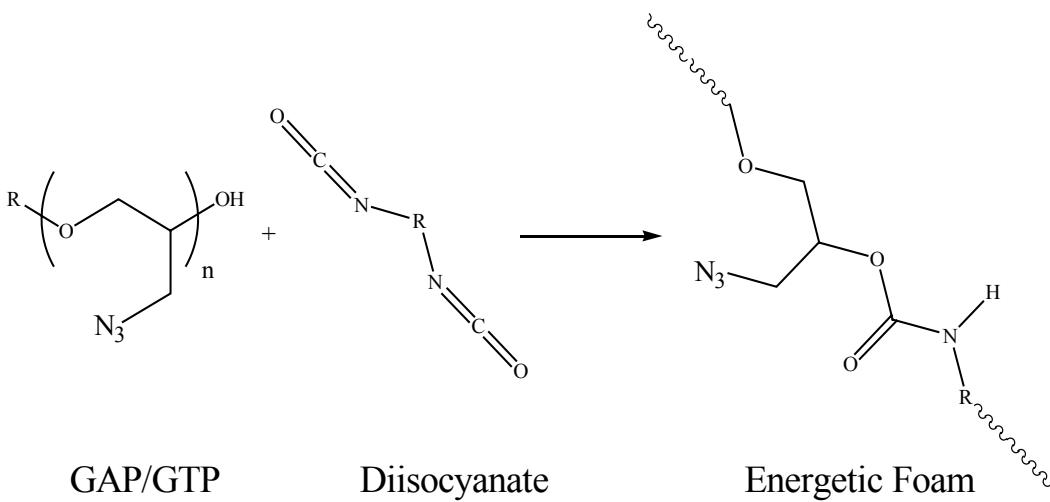
Figure 5-1.   A simple urethane linkage.

Aside from propellants and binders, energetic foams could also serve as transportable explosives. It may be possible to seal the foam in a canister so that soldiers could carry it in the field. The energetic foam could then be applied to doors, rocks, or any other obstruction that should be detonated (Energetic Materials Workshop, 2004).

Foams could also replace the propellant systems in air bags or other common applications (Hughes, *et al* 2000). The tunability of foams makes the number of applications virtually endless. Foams can be soft like shaving cream, compressible like a sponge, or very hard. To understand how this is possible, a general description of foams is necessary.

A foam is typically defined as a dispersion of gas bubbles in a liquid. They are lightweight and versatile and are used in a large number of applications. The solid phase of the foam is called the plastic matrix. The matrix consists of a base resin and other compounding ingredients. These other compounds include: plasticizers, stabilizers, cross-linkers, surfactants, dyes, pigments, fire retardants, or fillers. These compounds define the rigidity of the foam. Depending on the chemical composition of the starting materials, a foam can be flexible, semi-flexible, or rigid. Rigid foams have a glass transition temperature (T_g) above room temperature, while flexible foams have a T_g below room temperature (Blaga, 1974).

The gas bubbles constitute the other critical component of foams. Blowing or foaming agents are used to introduce the air bubbles into the plastic matrix. These can be divided into 3 distinct classes: chemical, physical, and mechanical (Wilson, 1989). However, current blowing agents are not limited to these classes (Roth A. J., 2003).

Chemical blowing agents are materials that are usually stable at room temperature, but—under certain conditions—undergo decomposition to produce gases. Ideally, this should be a very controllable process. These chemical blowing agents can be divided into 2 major classes: organic and inorganic. Inorganic blowing agents—such as sodium bicarbonate, ammonium carbonate, and sodium boron hydride—slowly generate gases and are difficult to control. Therefore, the inorganic agents are not widely used. Organic blowing agents however, are very popular. Gas can be generated predictably and easily using these agents. The organic nitrogen compounds are used most often. These compounds, like azodicarbonamide, produce mainly nitrogen gas (Wilson, 1989).

Although it does not fall completely within the realm of the chemical blowing agents, water is a well-known foaming agent. Water reacts with the isocyanate groups in the foam mixture to generate carbon dioxide through the mechanism shown in Figure 5-2. The carbon dioxide forms the gas bubbles that create the bubbles in the foam.

In addition to the chemical blowing agents, physical blowing agents are also used. Physical methods are unlike the chemical methods because the physical properties of the blowing agents do not change during use. The most common physical methods involve the expansion of a gas dissolved in a resin matrix by reducing the pressure. Another method is the boiling off of a low boiling liquid by either application of external heat or by harnessing the heat of the exothermic process.

The third and final method of gas creation is mechanical. In this method the foams are "whipped" with gases. The gases are trapped in the matrix as the foam
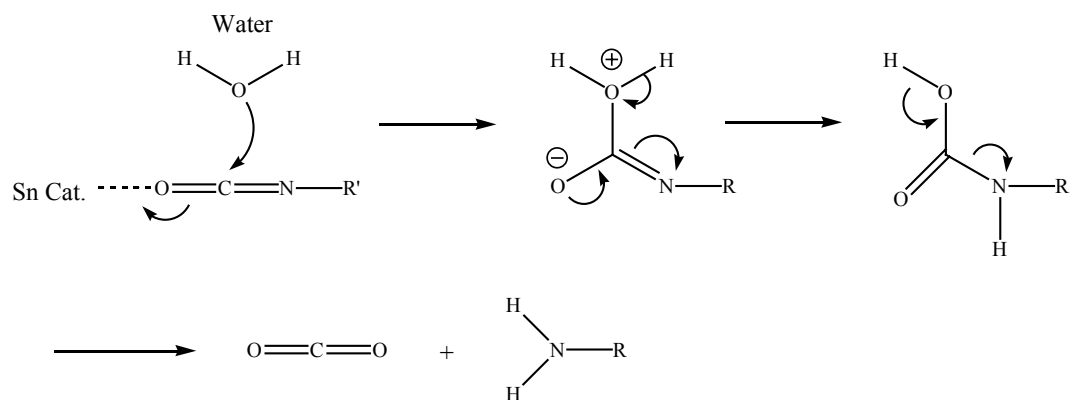
Figure 5-2.   The mechanism by which water reacts with the diisocyanate to generate the carbon dioxide bubbles in the foam.

hardens. This method is valuable because it creates consistently sized bubbles in the foam matrix (Wilson, 1989).

The goal of this research was to create a polyurethane based energetic foam. The energetic starting materials were the polymers synthesized in Chapters III and IV. The hydroxyl terminated chains allowed for the urethane linkages to be formed.

An extensive review of the literature yielded a great deal of information. It was learned that the combination of a hydroxyl-terminated polymer, a diisocyanate, and a tin catalyst formed the critical urethane linkages (Figure 5-1).

The tin catalyst used in these experiments was dibutyltin dilaurate. By complexing with the oxygen of the diisocyanate, the catalyst facilitated the attack of the carbon in the diisocyante by the terminated hydroxyl group of the polymer (Figure 5-3). For the diisocyanate, isophorone diisocyanate was chosen. This decision was made because of its availability and the fact that it was a liquid at room temperature.

The literature also revealed that the presence of a surfactant was necessary in all of these processes. Silicon based surfactants are very important in forming urethane foams. The mechanical properties of a cured polyurethane foam are greatly affected by the structure of the silicon surfactant. The bubble generation and cell window stabilization phase are both impacted by the surfactant. The role of the surfactant is to lower the surface tension at the air-polyol interface (Zhang, 1999). It is believed that silicon surfactants can lower surface tension, promote generation of bubbles during mixing, stabilize cell windows, and emulsify incompatible formulation ingredients. In this project, Dow 193 was chosen as the surfactant because of its common use in the literature. Studies show that the structure of the silicon polymer can affect air
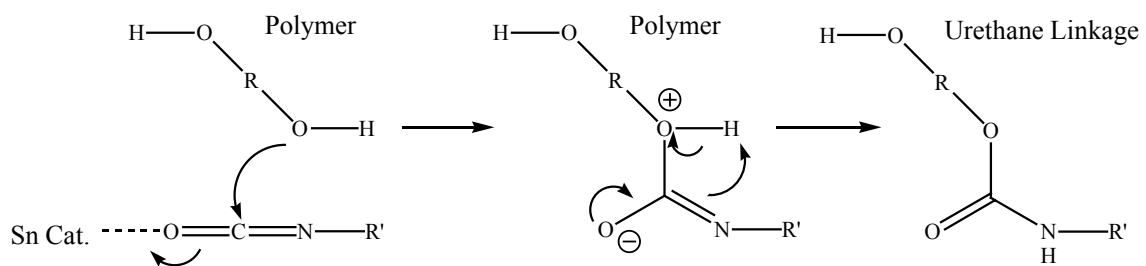
Figure 5-3.   The mechanism of the reaction between the hydroxyl-terminated polymer
and the diisocyanate. The tin catalyst used in this project was dibutyl tin
dilaurate.

permeability and foam cell size (Zhang, 1999). Therefore, to avoid inconsistencies, Dow 193 was used in all of these experiments.

The last decision that was made before the experiments were performed involved the choice of a blowing agent. Water was initially chosen because of safety concerns. The starting materials were explosive; and due to the exothermic nature of the urethane reaction, physical blowing agents were avoided because they would have required the use of an external heating source. A mechanical technique was also used to generate the energetic foams.

Experimental Methods

Materials

The chemicals used during these experiments were obtained and used without further purification or synthesized in the lab. The chemicals used included: glycidyl azide polymer (Chapter III), isophorone diisocyanate (Aldrich, 99%), Dow 193 (Dow, 99%), dibutyltin dilaurate (Aldrich, 99.9%), and water.

Procedure

For the reactions that created the gas bubbles chemically, a large culture tube was used to house the reaction. The reactants were loaded and a small magnetic stir bar was added. For the trifunctional polymers, the stirring was assisted with a wooden applicator. For the foams synthesis that used mechanical gas introduction, a mechanical overhead stirrer was used. A special blade was created with small holes that facilitated the "whipping" of the foam. The reactants were added and the stirring was commenced at

300 RPM until the foam had formed. GAP Foam: ^{1}H, δ (d-DMSO): 0.6-0.96 (s, 6H);

1.231 (s, 3H); 1.563 (s, 2H); 2.476 (s, 2H); 2.913 (s, 1H), 3.26-3.95 (m, 2H, 2H, H); ^{13}C,

δ (d-DMSO):   14.609 (3-CH$_3$), 21.998 (C), 22.756 (C), 26.458 (CH$_2$), 29.37 (CH$_2$),

31.859 (CH$_2$), 36.543 (CH), 51.71 (CH$_2$), 60.72 (CH$_2$), 69.57 (CH), 71.781 (CH2), 78.72

(CH$_2$). DSC plotted in the last figure of this chapter.

(Chemically produced foams) Glycidyl azide polymer (0.5g, 5.0 mmol) was added to the test tube. Isophorone diisocyanate (0.140g, 0.5 mmol) was then added. The tube was then secured in the fume hood and submersed in an ice bath. Dow 193 (0.012g) was then added followed by dibutyltin dilaurate (0.010g, 0.01 mmol). Water (0.012g) was then added to facilitate the gas creation. The mixture was then stirred in the ice bath until the foam stopped expanding and/or bubbling.

(Mechanically produced foams) Glycidyl azide polymer (0.5g, 5.0 mmol) was added to a 100 mL 3-neck flask. Isophorone diisocyanate (0.140g, 0.5 mmol) was then added. The tube was then secured in the fume hood and submersed in an ice bath. Dow 193 (0.012g) was then added followed by dibutyltin dilaurate (0.010g, 0.01 mmol). The mechanical stirrer was then activated and run at 300 RPM with the special stir blade. The process continued until the foam formed on the side of the reaction flask.

<u>Results and Discussion</u>

The initial reactions were run on a 0.5g scale. The reactants were loaded into a culture tube and placed in an ice bath. After the addition of the surfactant, the polymer and the isophorone diisocyanate created a creamy single phase. Water, the blowing agent, was always the last reactant that was added. Initially, the reactions were stirred with a wooden applicator before and after the addition of the water. The reaction took place very quickly (~30 seconds) and the stirring was continued until the bubbling stopped. For more consistent stirring, a magnetic stir bar was used in place of the applicator in the later experiments. This method was successful for the di-functional GAP, however, this method did not transfer successfully to the tri-functional GAP because of its high viscosity.

For all of these experiments, the conditions were kept static with the exception of the mol percent of isophorone diisocyanate. As expected, the foams synthesized with a higher mol percent were more rigid (Figure 5-4). The foams synthesized with 25 mol percent of the isophorone diisocyanate were crusty solids, while the foams made with 10 mole percent or less were very flexible. The cross linker was therefore critical in defining the physical properties of the foam.

As previously stated, chemical or physical blowing agents were avoided due to safety concerns. Mechanical means, however, did not impose any special danger. Therefore, a special stir blade was designed with the intention of introducing gas bubbles into the plastic matrix. This special paddle (shown in Figure 5-5) was a Teflon stir blade with a series of assymetrical holes drilled along its base.

<div align="center">

5   10   25
(mol percent of isophorone diisocyanate)

</div>

Figure 5-4.   The water blown foams made with 5, 10, and 25 mol percent of
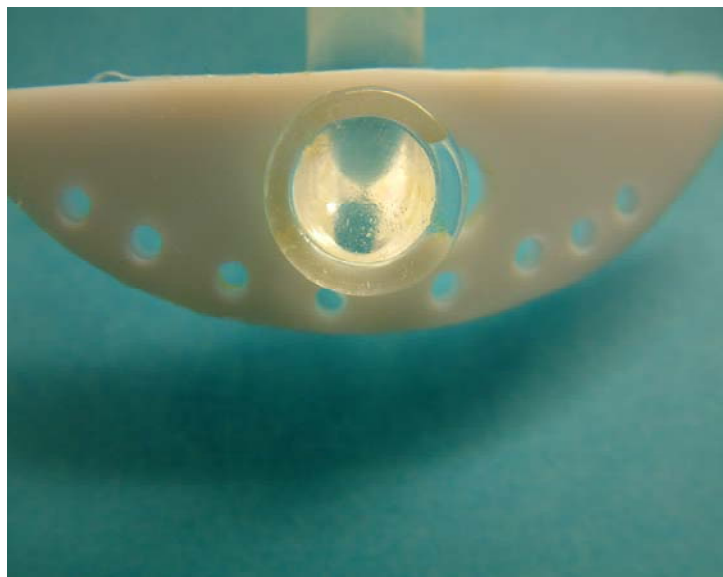isophorone are shown. All of these foams were made with difunctional
GAP.

Figure 5-5.   The stir blade used in an attempt to mechanically introduce air bubbles into the plastic matrix of the energetic foams.

These reactions were performed in the same manner as the reactions previously described with two major exceptions: water was not added and the reaction was run in a 3-neck round bottom flask. The water was not needed because the gas was to be introduced mechanically. The surfactant however was still present to assist in the mixing of the components, promote bubble growth, and to stabilize the foam. The foams made with this method had the physical characteristics of a rubber. It should be noted that the mechanical method only worked for the foam with 10 mol percent of diisocyanate (Figure 5-6). The mixture containing 5 mol percent of the diisocyanate failed to form the urethane linkages, while the formulation with 25 mol percent formed a clear, hard rubbery film on the sides of the flask.

After these experiments, the exothermic properties of the foams were tested using differential scanning calorimetry. The foam possessed an exotherm on par with the energetic polymer starting materials. The addition of the surfactant, catalyst, and water did little to diminish the energetic potential of the foam (Figure 5-7). The foam displayed in this figure was made with 25 mol percent of diisocyante and water generated air bubbles. This foam was chosen because its rigid character made it easy to place and weigh out into the DSC pan. Also, with 25 mol percent of diisocyante it was assumed that it would have the lowest exothermic potential.

Conclusion

The experiments in this chapter proved that urethane chemistry could be easily applied to glycidyl azide polymer to create energetic foams. These discoveries further illustrated the utility of these energetic polymers. The foaming of these polymers opened

Figure 5-6.   The foam on the right was produced with the mechanical stir blade, while the foam on the left was produced using magnetic stirring.

Figure 5-7. DSC curves for pure GAP, the energetic foam, and H-GTP.

up a limitless number of potential applications. By altering the characteristics of the starting material, the blowing agent, the surfactant, or the cross-linker, energetic foams can be tuned or altered in many ways. With the simple chemistry and limitless versatility outlined in this chapter, energetic foams could play a major role in the future of energetic materials.

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CHAPTER VI

THE SYNTHESIS AND CHARACTERIZATION OF ENERGETIC IONIC LIQUIDS

Introduction

Ionic liquids are molten salts that are dense liquids at or near room temperature. In addition to this feature, they exhibit no detectable vapor pressure. While known for decades, ionic liquids have recently experienced a rebirth as "new solvents" for environmentally benign chemical processes, reactions, and separations (Welton, 1999; Chauvin, *et al* 1995; Gull *et al* 2000). The majority of ionic liquids have molecular structures based on the imidazolium or ammonium cations along with an appropriate anion (Seddon, 1997; Holbrey, *et al* 1999; Huddleston, *et al* 2001). The physical properties of these species (melting point, boiling point, etc.) can be tuned either by changing the length of the alkyl chain attached to the nitrogen atoms or by changing the counter anion. Two structures of commonly used salts are shown in Figure 6-1.

Ionic liquids—due to their special characteristics—receive consideration as energetic materials in this chapter. Energetic materials are useful as propellants, gas generants, etc. One special class of propellants is called "monopropellants." A monopropellant is a chemical propellant that does not require a separate oxidizer. Hydrazine (N_2H_4) is currently considered the state of the art in the field of monopropellants, and has been studied for 30 years (Sutton, 1992). Hydrazine is decomposed by passing the compound through a heated bed of an iridium-coated alumina catalyst, providing ammonia, nitrogen, and hydrogen gas. The decomposition of hydrazine can be controlled to provide the volatile products in varying stoichiometries.
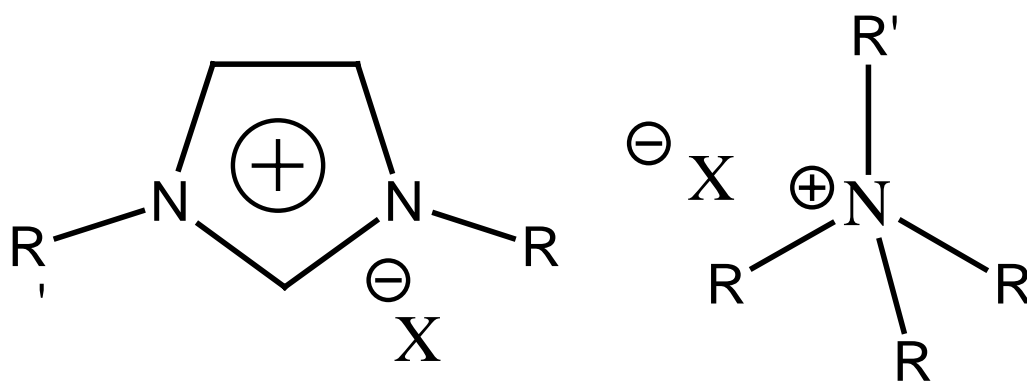
Figure 6-1.   Two generalized common structures for ionic liquids.

This feature allows the specific impulse to vary. As a result, the hydrazine systems are stable, dependable, and provide consistent and predictable results (Sutton, 1992).

Despite these advantages, hydrazine is plagued by several severe drawbacks. It is a potential carcinogen that damages living tissue. Hydrazine also has a very high vapor pressure. Workers must wear self-contained breathing suits to protect themselves from the toxic vapors. These safety concerns significantly raise the cost of working with hydrazine (Sutton, 1992). Ionic liquids would overcome these problems because of the lack of vapor pressure.

The goal of this research was to use tetrazole anions and cations instead of the imidazole moiety commonly used in ionic liquids (Figure 6-1). The energetic capability of the tetrazole group combined with the special properties of ionic liquids opened up a huge number of possibilities with regard to energetic materials.

The first phase of this research involved an extensive literature search on the imidazolium-based ionic liquids. The relationship between structure and properties of the imidazolium-based ionic liquids had been thoroughly studied. In Figure 6-2, the correlation between the length of the alkyl chain on the cations and the melting points of the corresponding ionic liquids is displayed (Holbrey, *et al* 1999; Welton, 1999; Wasserscheid, *et al* 2000). The dramatic influence that the length of the alkyl chain had on the properties of the ionic liquids clearly indicated the explicit tunablity of these compounds.

An extensive literature research was also performed on the tetrazole chemistry. An analogy between the melting points of the 5-methyltetrazole salts and the
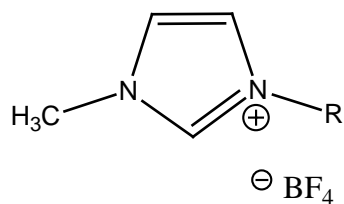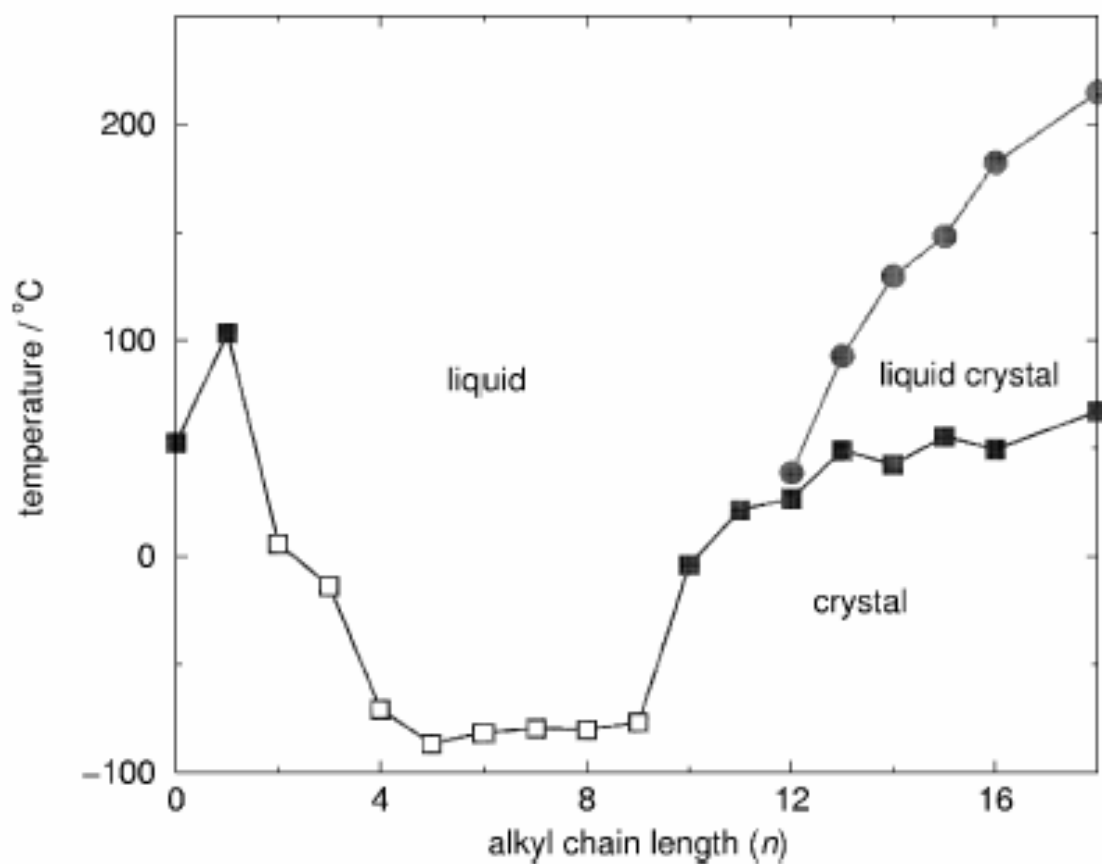
Figure 6-2.   The phase changes that the length of the alkyl chain induces on the
imidazolium based ionic liquid.

imidazolium salts was found (Borch, 1969; Lee, *et al* 1972; Hanley, *et al* 1979; Araki, 1983, Araki, 1984; Araki *et al* 1998). The reported melting points of the amine salts of 5-methyltetrazole (5-MT) decreased as the length of the alkyl chain on the ammonium cation increased and/or as a branched alkyl chain was introduced. The bis-ammonium salt of 5,5'-bi-1*H*-tetrazole (BHT) was studied as well; and, its trimethylammonium salt (Figure 6-3 and Table 6-1) exhibited a relatively low melting point (38°C) (Welton, 1999).   For each amine salt of the 5-methyltetrazole (5-MT) and 5,5'-bi-1*H*-tetrazole (BHT), the alkyl groups on the amine counter-part have been highlighted. Their importance will become clear later in this chapter. So far, no other cations have been studied.

Based on the research found in the literature, two classes of ionic liquids based on the tetrazole moiety were designed. Class I was composed of a negatively charged tetrazole coupled with a variety of tetra-alkyl ammonium cations. Class II was composed of a positively charged tetrazole coupled with a variety of counter anions (Figure 6-4.). Classes I and II provided the basis for the development of new liquid propellants with unique physical properties. The experiments performed to synthesize these new compounds were analogous to those found in the literature for the imidazolium compounds (as tetrazoles have not been widely used to produce ionic liquids).

The R_1, R_2, and R_3 on the amine counterpart allowed for an infinite number of combinations. However, it was important to keep in mind the trends observed for the imidazolium ionic liquids in order to consider only the most promising associations. The symmetry, the 'greasy' character (the length of the alkyl chains), and the basicity of the
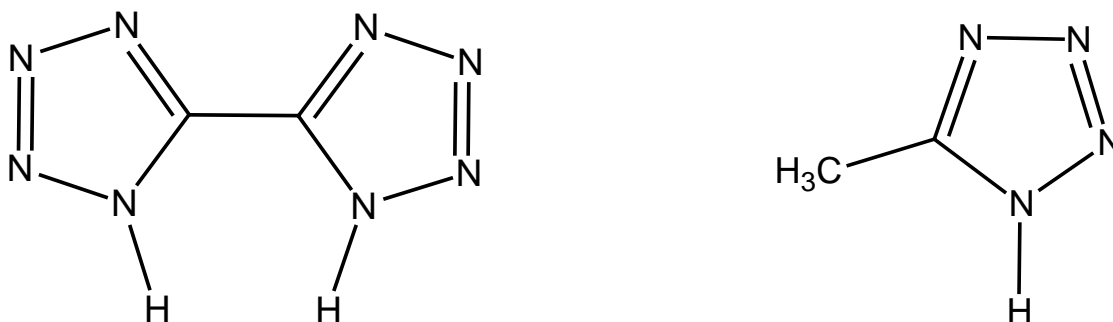
Figure 6-3   5,5'-bi-1*H*-tetrazole (**BHT**) (Left) and 5-methyltetrazole(5-**MT**) (Right).

Table 6-1.   Literature reported melting points for BHT and 5-MT amine salts.

Amine Salt of	Amine counter-part	Mp (^{o}C)
BHT	Tri**methyl**amine (Bis Salt)	38
5-MT	Di<u>**methyl**</u>amine	90
5-MT	Di**ethyl**amine	70
5-MT	Iso**propyl**amine	58

Figure 6-4.   The Class I (left) and Class II (right) tetrazole based ionic
               liquids.

amines were carefully balanced to obtain a molten salt state. Six amines were selected with different alkyl chains, symmetry, and substitution patterns (Table 6-2).

<div align="center">Experimental</div>

Materials

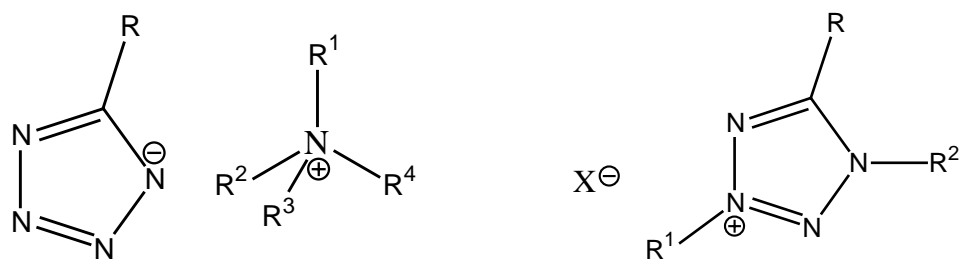The chemicals used in these experiments were purchased from Aldrich and used without additional purification.   The chemicals used included the following: 5-methyltetrazole (Aldrich, 99.9%), methanol (Aldrich, 99.9%), N,N-dimethylbutylamine (Aldrich 99%), Isopropylamine (Aldrich 99.9%), Diisopropylamine (Aldrich 99.8%), Butylamine (Aldrich 99.7%), Pentylamine (Aldrich 99%).

Procedure

The 5-methytetrazole (0.5g, 6.0 mmol) was placed in a round bottom flask equipped with a temperature monitoring system. The methanol (5 ml) was added and the solution was stirred at 0°C for 5 min. The amine (1.1 eq) was added drop-wise in order to control the exothermic reaction. At the end of the exotherm, the reaction was heated for 2h at 65°C. The reaction was then cooled to room temperature. High vacuum was then applied to remove the methanol and un-reacted amine. The resulting product (quantitative yield) was analyzed by ^{1}H NMR (d-DMSO). N,N-dimethylbutylamine ionic liquid, ^{1}H, δ(d-DMSO): 0.86 (t, 3H, CH_3), 1.27 (st, 2H, CH_2), 1.56 (m, 2H, CH_2), 2.46 (s, 6H, CH_3), 2.68 (s, 3H, CH_3), 2.92 (m, 2H, CH_2). Mp = 101.3^{o}C (dcp). Isopropylamine ionic liquid,

Table 6-2.   The six selected and tested amines and their alkyl chain/substitution
            pattern.

Amine	R_1 Group	R_2 Group	R_3 Group
Amylamine	-$(CH_2)_4CH_3$	-H	-H
Butylamine	-$(CH_2)_3CH_3$	-H	-H
N,N-dimethylbutylamine	-$(CH_2)_3CH_3$	-CH_3	-CH_3
Isopropylamine	-$CH(CH_3)_2$	-H	-H
Disopropylamine	-$CH(CH_3)_2$	-$CH(CH_3)_2$	-H
Triisopropylamine	-$CH(CH_3)_2$	-$CH(CH_3)_2$	-$CH(CH_3)_2$

^{1}H, δ(d-DMSO): 0.91 (d, 6H, CH$_3$), 1.86 (sept, 1H, CH), 2.25 (s, 3H, CH$_3$), 2.66 (d, 2H, CH$_2$), 6.36 (b, 3H, NH). Mp = 109.9^{o}C. Diisopropylamine ionic liquid, ^{1}H, δ(d-DMSO): 1.20 (d, 12H, CH$_3$), 2.25 (s, 3H, CH$_3$), 3.31 (m, 2H, CH). Mp = 121.6^{o}C. Butylamine ionic liquid, ^{1}H, δ(d-DMSO): 0.86 (t, 3H, CH$_3$), 1.32 (m, 2H, CH$_3$), 1.58 (m, 2H, CH$_2$), 2.29 (s, 3H, CH$_3$), 2.89 (t, 2H, CH$_2$). Pentylamine ionic liquid, ^{1}H, δ(d-DMSO): 0.85 (t, 3H, CH$_3$), 1.27 (m, 4H, CH$_2$), 1.56 (m, 2H, CH$_2$), 2.23 (s, 3H, CH$_3$), 2.79 (t, 2H, CH$_2$).

<div align="center">Results and Discussion</div>

The first compounds synthesized were the Class I ionic liquids seen in Figure 6-4. The groups R, R$_1$, R$_2$, R$_3$, were changed in order to induce a liquid state at room temperature (i.e. low melting point). Since the 5-MT was reported in the literature and was commercially available, the effort focused on the salts of this compound. Therefore, the R group in the 5-position on the tetrazole ring was assigned as a methyl group. The proton on the nitrogen in position 1 on the 5-methyltetrazole was relatively acidic and reacted with bases--such as amines--to form the corresponding ionic species. The simple acid/base reaction was successfully applied to prepare the 5-methyltetrazole molten salts (Figure 6-5).

The reaction conditions were optimized to yield quantitative completion. Since all the selected amines were liquid at ambient conditions, the first attempt was conducted without the use of a solvent (neat). This option made a simple work-up possible and increased the efficiency of the reaction. The amine was placed into the reaction flask and
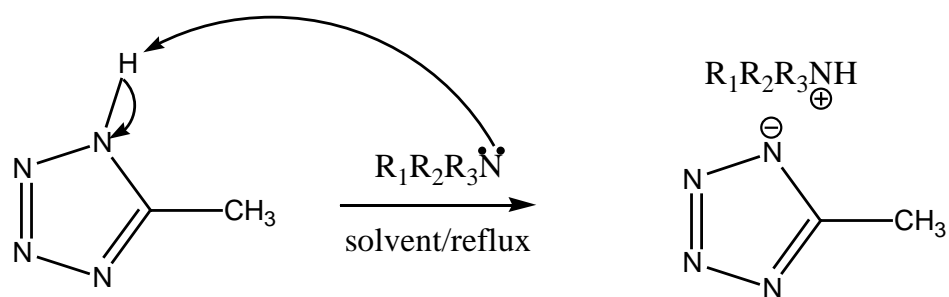
Figure 6-5.   Acid/Base reaction used to synthesize 5-methyltetrazole (5-MT) salts.

the solid 5-methytetrazole (mp: 142-146°C) was carefully added. Soon after the addition, an exotherm ($> 40^{o}$C) was observed. The exotherm raised awareness about safety and reaction control. The reaction conditions were therefore modified and a solvent was introduced. The solvent was carefully chosen to allow for a simple purification as well as maximum reaction efficiency (miscibility, medium polarity etc.). After careful consideration, methanol was chosen as the solvent. However, the dilution of the reactants was strictly monitored and minimized. With the use of the solvent, the reaction was successfully carried out with only a slight exotherm.

It was essential for these reactions to reach completion since there were no purification techniques that could easily be applied to these systems. In the case of highly substituted amines—such as diisopropylamine and triisopropylamine—the reaction did not reach completion like the mono-substituted amines (e.g. butylamine). The basicity and steric hindrance of the substituted amines slowed the rate of the reaction. To reach completion (according to the literature), the reaction mixture must be heated for 2h at 65°C after the disappearance of the initial exotherm. Accordingly, each reaction was carried out using this procedure to insure complete conversion regardless of the reactivity of the amine. Due to the energetic potential of these systems, all reactions were carefully placed behind safety shields. In addition, solvent removal was not performed on the usual rotary evaporator apparatus. High vacuum was directly applied to the reaction mixture in order to remove all the solvent (methanol) and the excess amine. The chosen panel of amines produced significant information concerning the structure/properties relationship of the tetrazole-based ionic liquids (Table 6-3).

Table 6-3.   Amine salts of 5-methyltetrazole (5-MT). The substitution pattern as well
               as the properties (mp, density) are reported.

Amine	R$_1$ Group	R$_2$ Group	R$_3$ Group	Aspect	characteristic
Amylamine	-(CH$_2$)$_4$CH$_3$	-H	-H	Liquid/ amber	d=1.00+/-0.1 g/ml
Butylamine	-(CH$_2$)$_3$CH$_3$	-H	-H	Liquid/ beige	d=1.00+/-0.1 g/ml
N,N-dimethylbutyl amine	-(CH$_2$)$_3$CH$_3$	-CH$_3$	-CH$_3$	Solid	mp(dcp)=101.3^{o}C
Isopropyl-amine	-CH(CH$_3$)$_2$	-H	-H	Solid	mp(dcp)=109.9^{o}C
Disopropylam ine	-CH(CH$_3$)$_2$	-CH(CH$_3$)$_2$	-H	Solid	mp(dcp)=121.6^{o}C
Triisopropyl-amine	-CH(CH$_3$)$_2$	-CH(CH$_3$)$_2$	-CH(CH$_3$)$_2$	--	No reaction occurred

These results further elucidated the critical role played by the substitution pattern of the amine. Regardless of the conditions, the trisopropylamine did not undergo reaction with the 5-aminotetrazole. This was attributed to steric hindrance. The branched amines (e.g. isopropylamine and diisopropylamine) yielded solid salts with melting points above 100°C. The tertiary amine – N,N-dimethylamine –also afforded a solid with a melting point near 100°C.

Nevertheless, the Class I tetrazole-based ionic liquids were successfully obtained when the straight chain mono-substituted amines were used (butylamine (**A**) and amylamine (**B**)).

The first phase of this research focused on synthesizing the Class I ionic liquids, while the second phase focused on evaluating the energetic potential of the ionic liquids. Two complementary approaches were adopted: theoretical and experimental. The theoretical approach—completed using SPARTAN—was based on *ab initio* calculations which allowed the identification of the lowest energy (most stable) conformers and their relative energy. This method was applied to both ionic liquids using Hartree-Fock (3.21G*) and density functional (B3LYP – 3.21G*) data sets. From the lowest identified energy, the enthalpies of formation were calculated based on isodesmic equations. Using the known enthalpy of formation, the energy impulses were simulated using a Chemical Equilibrim and Applications code (CEA) (Gordon *et al.*, 1994). The parameters involved in the simulation programs were the following: the oxidant was Inhibited Red Fuming Nitric Acid (IRFNA), the temperature was 298.15 K, the chamber pressure was 2000 psia, the pressure ratio (p_i/p) was 136.0919, the density was introduced if known (if the density was unknown it was estimated to be 1), and finally the ratio oxidant fuel (O/F)

was varied in order to determine the maximum performance. The same process was used for all the theoretical calculations in this research (including energetic polymers, ionic liquids, amines, and gels).   The densities of the ionic liquids measured in the laboratory were entered to obtain accurate energy impulse predictions. The energy density impulse simulations were essential because of the importance of developing highly dense energetic materials. Figures 6-6 and 6-7 were designed to illustrate the energy impulse (Isp) and density energy impulse (D*Isp) versus the O/F ratio for the energetic ionic liquids and other comparable materials. The ionic liquid performances were compared to the performances of well known propellants or energetic candidates: monomethyhydrazine (MMH, red), N,N-dimethylaminoethylazide (DMAZ, pink). The density impulse versus the O/F ratio plots demonstrated that the ionic liquids were comparable to other propellants with regard to density energy impulse.

Experimentally, differential scanning calorimetry (DSC) data was collected for the ionic liquids. (Figure 6-8). The exotherms were normalized to provide comparable values. An exotherm was observed for both butylammonium-5-methyltetrazolide (**A**) and pentylammonium-5-methyltetrazolide (**B**) salts at about 275°C. Respectively, the normalized exotherm values were 218 J/g and 147.5 J/g. Although both liquids displayed an exotherm, the normalized values were much smaller than the size of the exotherm for glycidyl azide polymer (GAP) which was 2100 J/g.

It should be noted that the exotherm produced by ionic liquid A was greater than the exotherm observed for B. This result was attributed to the longer alkyl chain on the B anion which lowered the ratio of energetic to non-energetic components. The exotherm values clearly reflected the loss of energy. Therefore, the ammonium counter anions

Figure 6-6.   The specific impulse [Isp (lb/s)] versus the oxidizer/fuel ratio [O/F
ratio] for the novel energetic ionic liquids and other common
energetic materials. (IRFNA is the oxidant).

Abbreviations

MMH – monomethylhydrazine
DMAZ – dimethylethylamino azide
BAMT – butylammonium-5-methyltetrazolide
ABAMT- pentylammonium-5-methyltetrazolide
1AEMT – 1-ethyl-3-pentyl-5-methyltetrazolium chloride
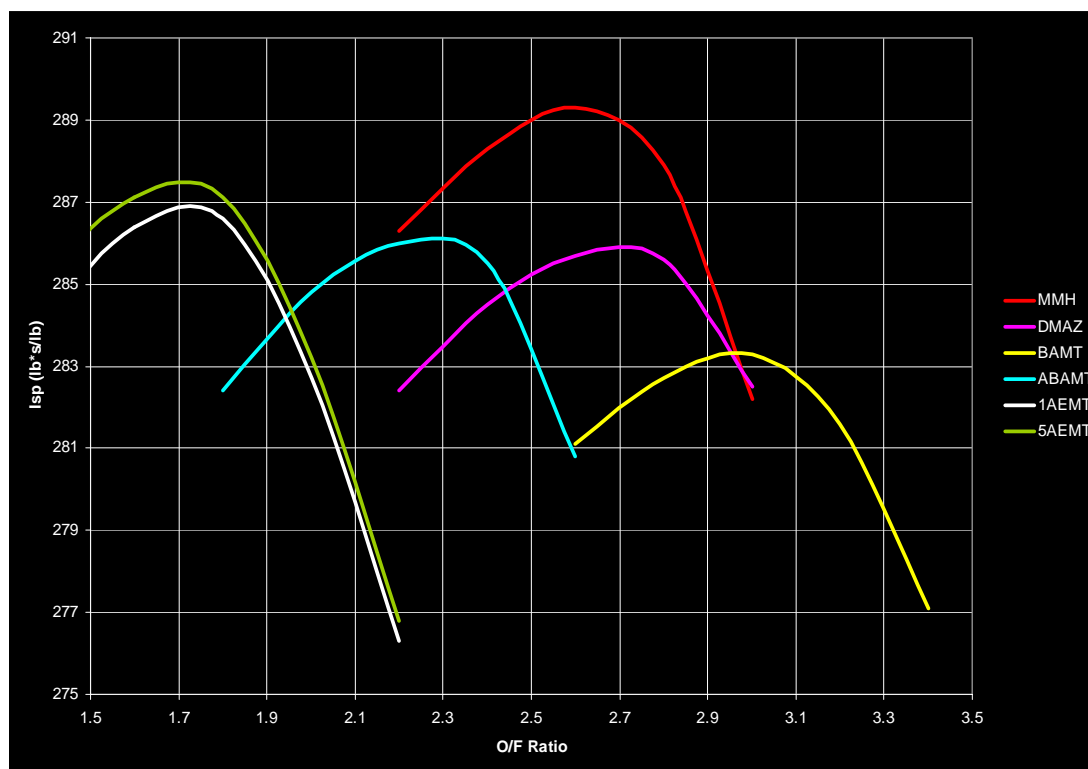5AEMT – 3-ethyl-1-pentyl-5-methyltetrazolium chloride

Figure 6-7.   The density energy impulse [D*Imp (lb/s)] versus the oxidizer/fuel ratio [O/F ratio] for the energetic ionic liquids and other common propellants.

Abbreviations

MMH – monomethylhydrazine
DMAZ – dimethylethylamino azide
BAMT – butylammonium-5-methyltetrazolide
ABAMT- pentylammonium-5-methyltetrazolide
1AEMT – 1-ethyl-3-pentyl-5-methyltetrazolium chloride
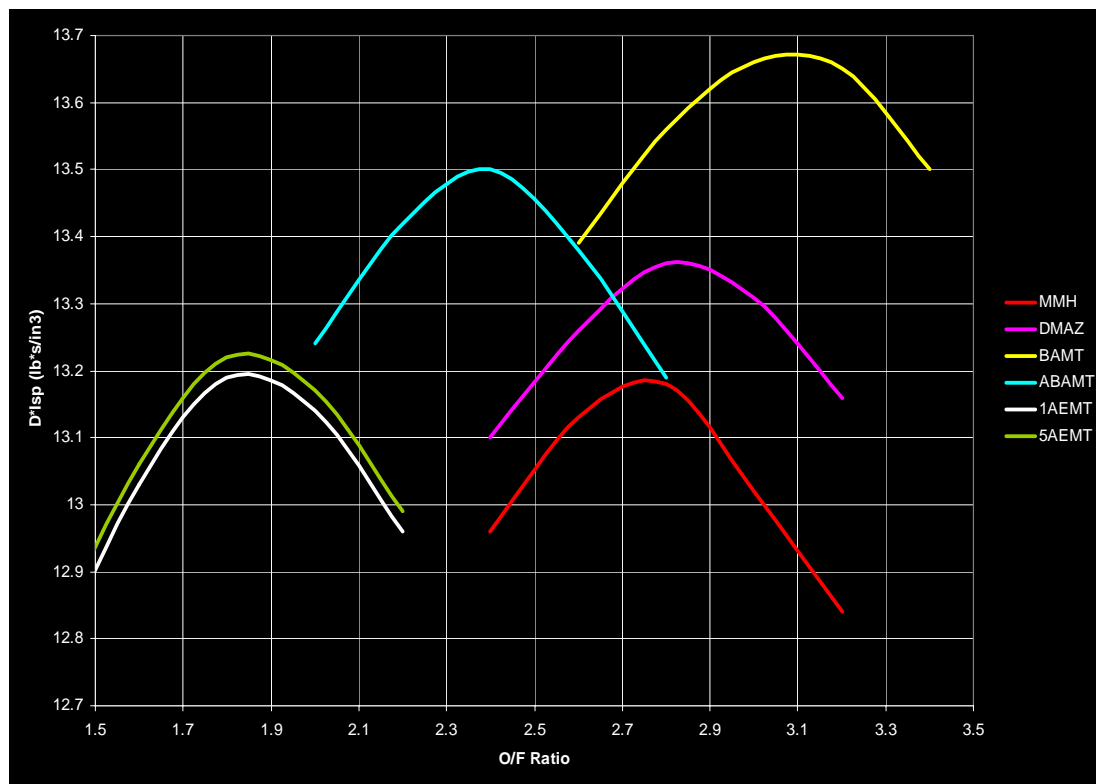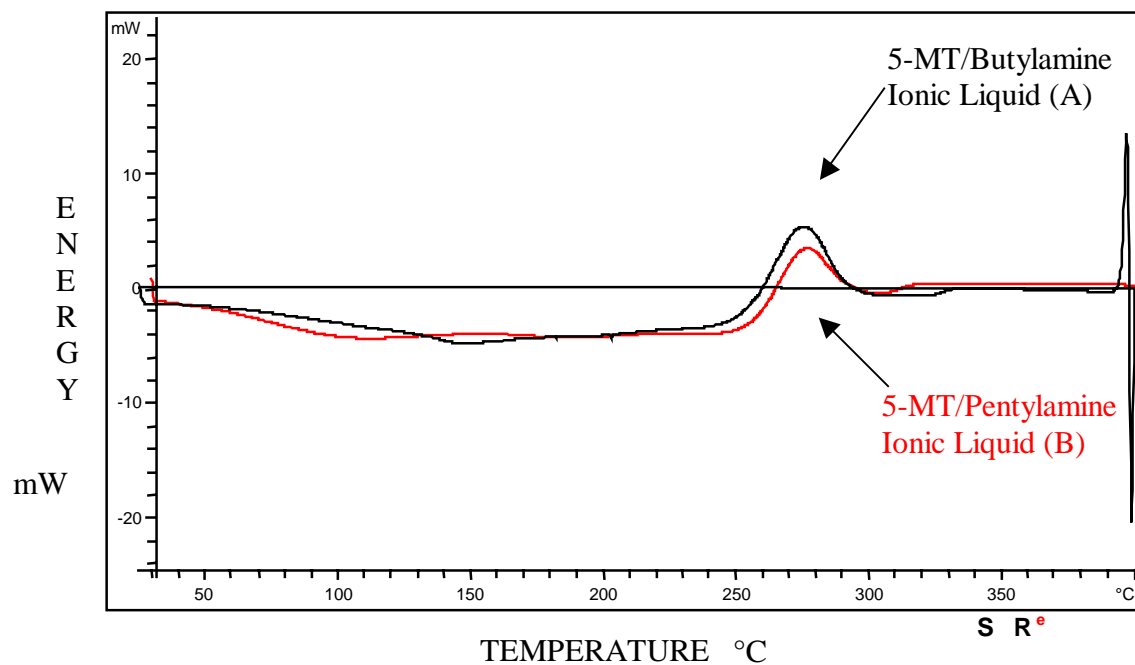5AEMT – 3-ethyl-1-pentyl-5-methyltetrazolium chloride

Figure 6-8.   DSC spectrum for the butylamonium-5-methyltetrazolide (A) and the amylammonium-5-methyltetrazolide (B) ionic liquids.

played a critical role in determining both the physical properties and the energetic potential of the ionic liquid. These plots demonstrated the importance of choosing the proper cation/anion combination.

Another opportunity that the ionic liquids offered was the unique ability to dissolve both ionic and organic species (Welton, 1999; Chauvin et al 1995; Blanchard et al, 1999). This property was exploited to increase the energy potential of the tetrazole-based ionic liquids. Energetic salts were dissolved into the ionic liquids to produce a highly energetic and dense solution. The energetic salts that were used included perchlorates and nitrates. Two perchlorates were tested: ammonium perchlorate and potassium perchlorate. As for the nitrate salts, sodium nitrate was used. Both ionic liquids A and B were used in these experiments (Table 6-4).

The salts were added to the ionic liquids in small increments (~10 mg) and the mixture was slowly stirred until dissolution was observed. The addition of the salts was stopped as soon as the liquids were saturated. The amount of each solid salt needed to saturate 1g of each ionic liquid was recorded (Table 6-4).

The DSC spectra of the saturated solutions were recorded to evaluate the exotherm enhancement. The ionic liquids with potassium perchlorate (Figures 6-9 and 6-10) exhibited an endotherm at ~120°C and an exotherm at ~275°C. For the butylammonium 5-methyltetrazolide and amylammonium 5-methyltetrazolide ionic liquids, the exotherm value remained low compared to GAP—128 J/g and 103 J/g, respectively. The saturated solutions of ammonium perchlorate in both tetrazole-based ionic liquids were also studied (Figure 6-11 & 6-12). The results were significantly

Table 6-4.   Amount of NH_4ClO_4, $NaClO_4$, and $NaNO_3$ needed to reach the saturation of 1g of ionic liquid A and B.

	5-MTButylamine Salt (1g)	5-MTAmylamine Salt (1g)
Ammonium Perchlorate	0.19 g	0.15 g
Potassium Perchlorate	0.19 g	0.15 g
Sodium Nitrate	<0.028 g	<0.02 g

Figure 6-9.   DSC spectrum of the saturated solution of **KClO₄** in butylammonium 5-methyltetrazolide (Bu-5-MT).

&AMYL IL KCIO4
AMYL IL KCIO4, 6.0000 mg

Integral	617.53 mJ
normalized	102.92 Jg^-1
Onset	255.49 °C
Peak	270.82 °C
Endset	285.86 °C

Integral	-559.65 mJ
normalized	-93.27 Jg^-1
Onset	74.02 °C
Peak	117.82 °C
Endset	121.74 °C

Lab: METTLER

STAR^e SW 8.00

°C

Figure 6-10.   DSC spectrum of the saturated solution of KClO$_4$ in amyl-
ammonium 5-methyltetrazolide (Bu-5-MT).

different from the potassium perchlorate results (Figure 6-9 & 6-10). In the case of the saturated solution of ammonium perchlorate in butylammonium 5-methyltetrazolide (Figure 6-11), the base line was steady and the exotherm was dramatically enhanced. Accordingly, the normalized value for the exotherm was 1307 J/g. The saturated solution of ammonium perchlorate in the amylammonium based ionic liquids (Figure 6-12) exhibited a similar base line and enhancement profile. The normalized value for the overall exotherm was 939 J/g. In addition to these results, the origin of the peaks at 290° C and 330°C will be explored in future experiments. Overall, the energetic ionic liquid solutions were highly energetic when the nitrates and perchlorates were dissolved in them. The exotherms of 1307 J/g and 939 J/g approached the GAP and the H-GTP exotherm values (2100 J/g and 1420 J/g, respectively).

Conclusion

The energy potential of the tetrazole based ionic liquids was demonstrated. For the first time, energetic molten salts from tetrazole derivatives were prepared. Tetrazole-based ionic liquids are dense materials that can be tuned and altered to produce high amounts of energy. The high density and the ability to dissolve energetic salts will be a key advantage for advanced propellants applications. Overall, the theoretical estimations and experimental data collected for both ionic liquids proved that these compounds could potentially replace many current energetic materials. With their tunability, non-existent vapor pressure, and high density, ionic liquids have many characteristics in common with the "ideal" propellant. These preliminary experiments prove that ionic liquids have significant potential in the realm of energetic materials.
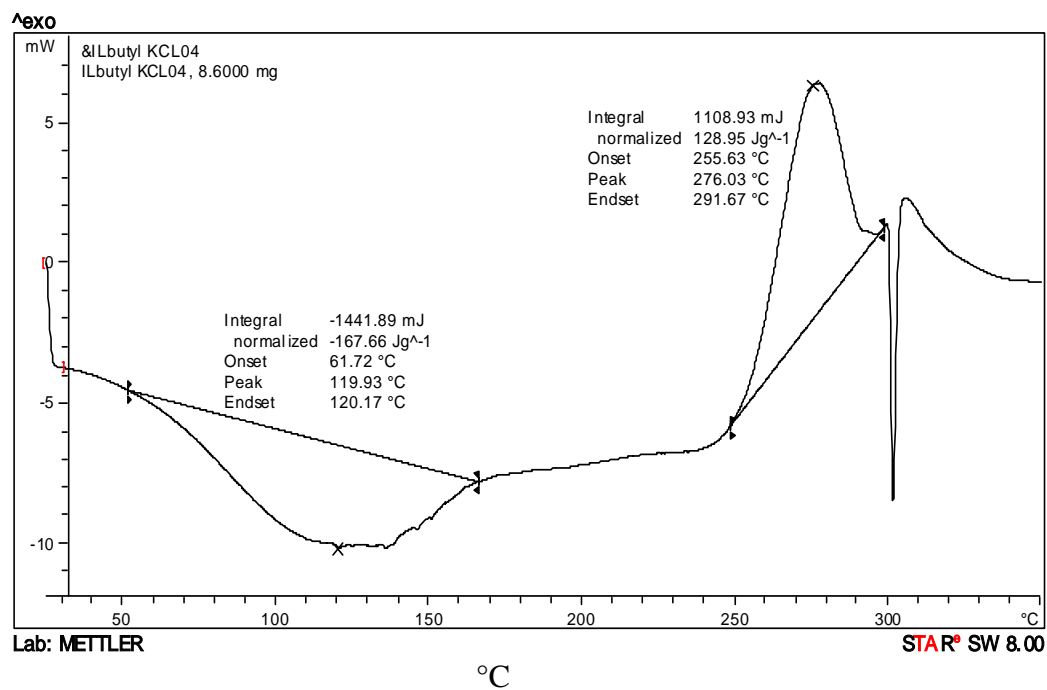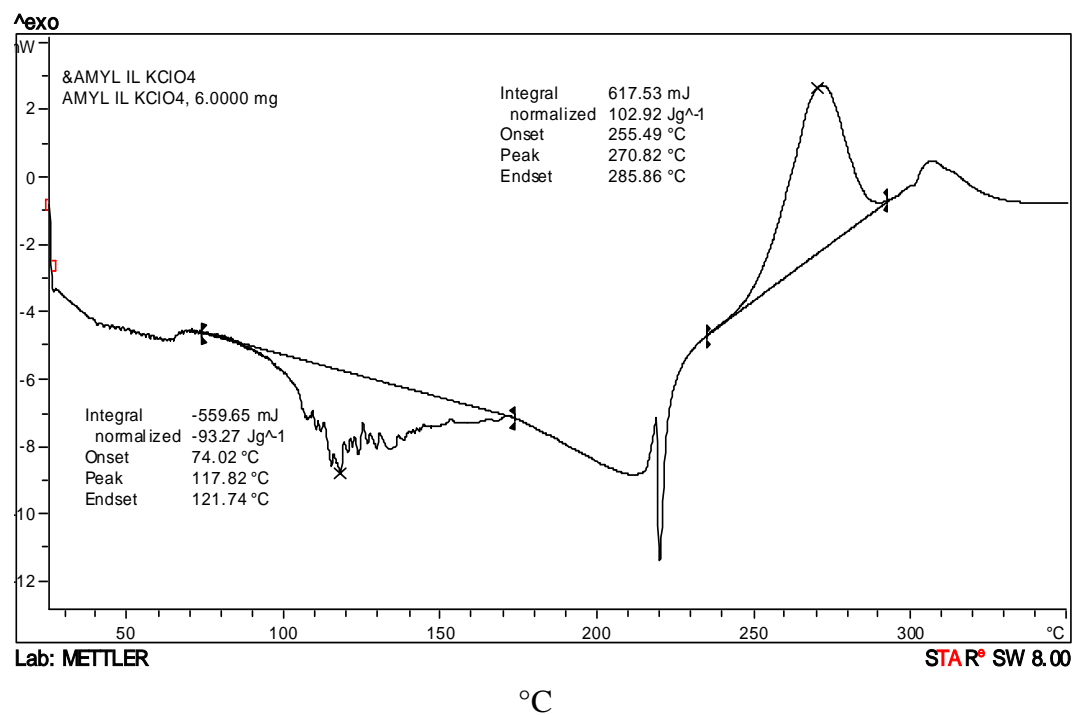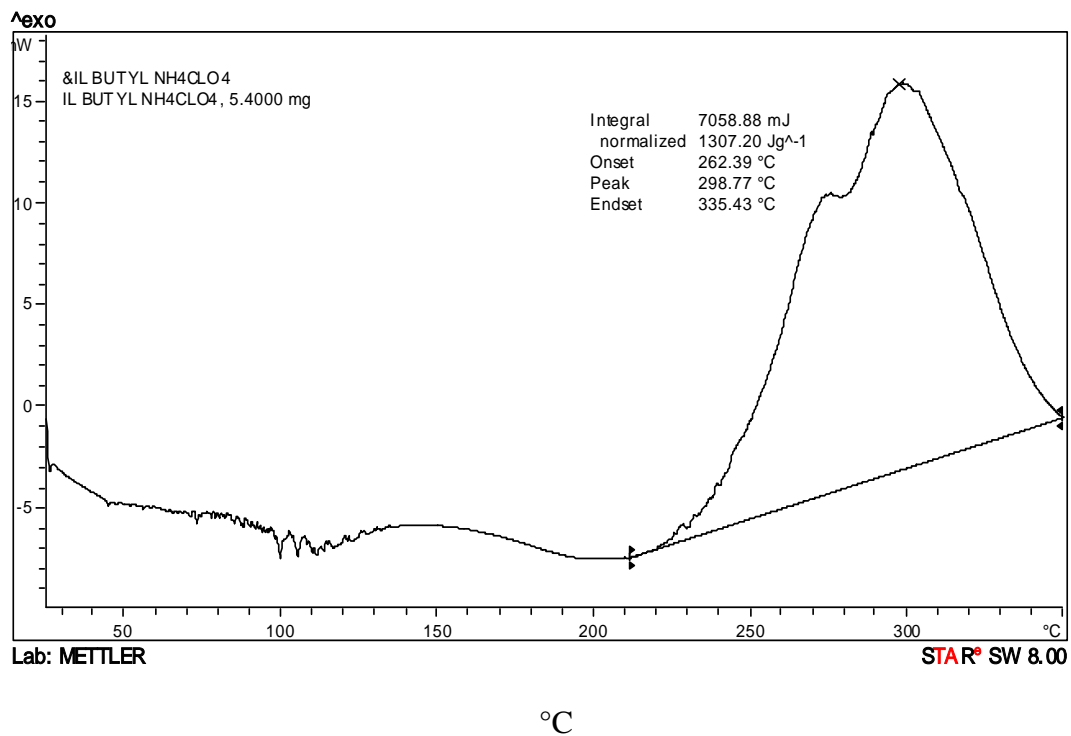
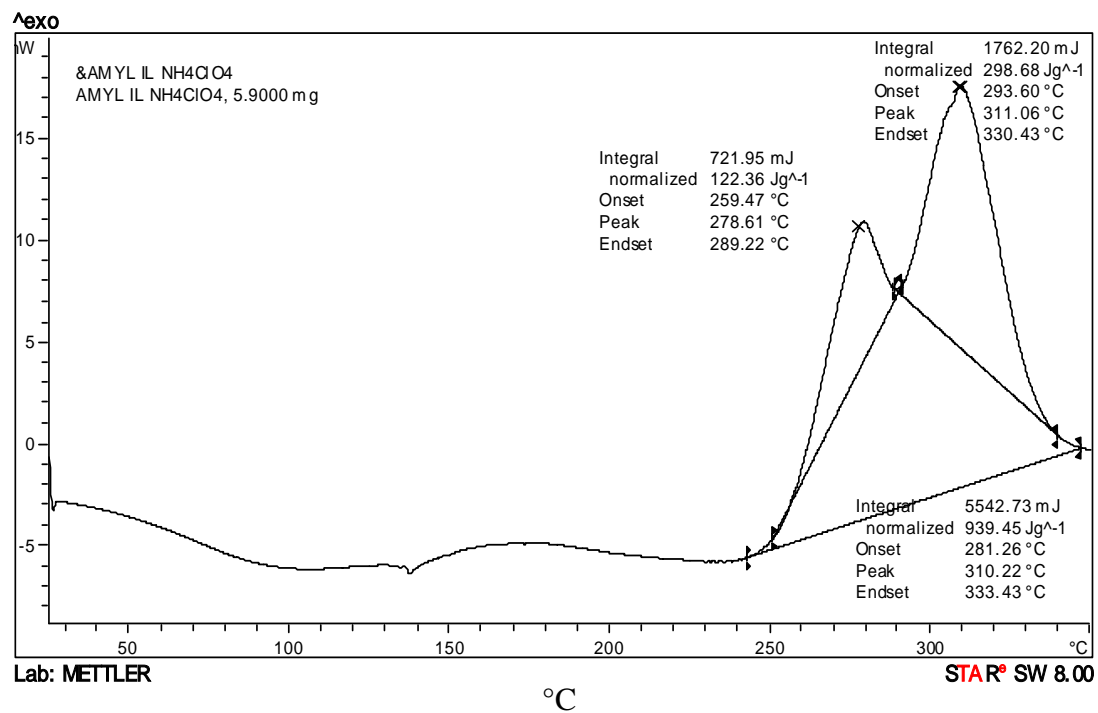Figure 6-11.   DSC spectrum of the saturated solution of **NH₄ClO₄** in butyl-ammonium 5-methyltetrazolide (Bu-5-MT).

Figure 6-12.   DSC spectrum of the saturated solution of NH_4ClO_4 in amyl-ammonium 5-methyltetrazolide (Bu-5-MT).

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CHAPTER VII

THE SYNTHESIS AND CHARACTERIZATION OF NOVEL ENERGETIC GELS

Introduction

The possibility of synthesizing an energetic gel has attracted a great deal of attention in the energetic materials community. The physical properties of gels allow them to share the advantages held by solid and liquid propellants. Gels have the potential to replace the current propellants used in rocket motors and other applications.

Solid propellants are useful because of their high density and uniform burning characteristics. Liquid propellants allow for a motor to be shut off or weakened unlike their solid counterparts. Because of their hybrid nature, gels would enjoy both of these qualities.

The thixotropic nature of gels also makes them safer to use. A thixotropic substance is one that will move or flow if a force is applied, but will act as a solid when it is stationary. (Toothpaste is an example of a thixotropic substance). If a large motor containing a gel is ruptured, the material would remain inside the canister. This would not be true for conventional liquids. Also, energetic gels—depending on the design— could be demilitarized with a simple aqueous wash. These properties are most inviting considering the modern age of terrorism (Energetic Materials Workshop, 2004).

This research focused on developing an organic and energetic three-dimensional network to create a gel and/or confer thixotropic properties to an appropriate liquid. Gels have been well studied in the energetic field, however, most of the research has focused on inorganic gels. Most of the work found in the literature concentrated on the gelation of known liquid monopropellants. For example, monomethylhydrazine (MMH) was treated

with an inorganic (silicon based) gelling agent (Pekala, 1998; Simpson, 1999; Tappan, 2002; Tillotson, 1998). The monomethylhydrazine is a highly efficient propellant. MMH has a very low flash point (38°F) and is extremely volatile. This high volatility makes this particular monopropellant especially hazardous to workers. The gelation of monomethylhydrazine (MMH), however, resulted in a dramatic depletion of the volatility and the safety hazards. Unfortunately, the gelling agent used was non-energetic and affected the performance of the final material. Some energetic gelling agents, like nitrocellulose, were used; but, the performance of these energetic gels still fell short of the propellant community's expectations.

By creating gels based on the tetrazole chemistry outlined in this thesis, this research was performed with the hopes of designing a high-performance energetic gel. The literature on the conventional gels was used as a guide for this research (Allcock, 1993; Cohen, 1996; Fried, 2003; Gevalda, 2002)

A tetrazole gel was reported in the literature as an alternative for polyester in a water adsorption application (Fried, 2003; Gavalda, 2002; Cohen, 1996; Allcock, 1993). This example was used as the foundation to develop a tetrazole based three dimensional (3-D) network from methacryloyl chloride that could be used in advanced propellant applications.

In the literature these polymeric materials were tuned by modifying the chemical structure of the monomer, the structure of the network, the molecular weight and/or the polydispersity of the polymer. It was expected that the proton in position 1 on the tetrazole ring would dramatically impact the physical properties of the materials. Due to hydrogen bonding, it was believed that the material would be a solid regardless of the

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other factors such as molecular weight. Therefore, it was proposed that the removal of the hydrogen with an amine would lower the melting point of the material. The ideas from Chapter VI were applied to the monomers and polymers presented in this chapter. The addition of the tetrazole to the monomer provided another tunable entity through which the polymers were adjusted

Experimental

Materials

The chemicals used in these experiments were purchased and used without additional purification. The chemicals used in these experiments included: methacryloyl chloride (Aldrich 99.9%), 5-aminotetrazole monohydrate (Aldrich 98%), tetrahydrafuran (Aldrich, 99.9%), 2,2'-azobisisobutyronitrile (Aldrich 99.99%), DMF (Aldrich 99.9%), DMSO (Aldrich 99%), hydrochlorydric acid (Aldrich 99.99%), butylamine (Aldrich 99%), pentylamine (Aldrich 99.98%).

Procedure

Synthesis of 5-(methacrylamido)tetrazole (Monomer I). Methacryloyl chloride (10.7g, 1.1eq) was added dropwise to a suspension of 5-aminotetrazole monohydrate (10.0g, 0.95mol) in THF (250 ml) and water (12ml) at room temperature. The solid dissolved after 30 min. Then after 1h, a precipitate appeared again. The reaction was then diluted with water (250ml), and stored overnight in a refrigerator. The white solid was collected by filtration in 60 % yield and placed in a vacuum oven (T = 40-50°C) for at

least one day. ^{1}H NMR δ(d-DMSO, ppm): 1.95 (s, 3H, CH$_3$), 5.72 (m, 2H, CH$_2$), 6.08 (m, 1H, CH), 11.95 (br, 1H, NH). Mp = 135.2^{o}C (dcp).

2-D Polymerization.   A solution of monomer I (2.00g, 13.1 mmol) and 2,2'-azobisisobutyronitrile (AIBN) (20mg, 0.12mmol) in DMF (20ml) was degassed for at least 3 hours. The reaction was heated to 65°C overnight. The reaction was cooled to room temperature and added drop-wise to a solution of methanol (250ml) and hydrochlorydric acid (5ml). The colorless solid was collected by filtration, washed with methanol and dried in vacuum oven (T^o = 40-50°C) overnight. The product was obtained in quantitative yield. Solid ^{13}C NMR δ (ppm): 20 (CH$_3$), 45 (CH$_2$), 50 (C), 150 (C tetrazole), 180 (C=O). Mp > 300°C.

3-D Polymerization. The monomer I (2.00g, 13.1 mmol) was added to a solution of sodium hydroxide (0.62g, 1.2 eq) in methanol (25ml) and was refluxed for 5 min. After the solvent was removed on a rotary evaporator, the residue was dissolved in deionized water (10ml) and 2,2'-azobis(2-methylpropionamidine) dihydrochloride (V-50)(20.1mg, 0.074mmol) and N,N'-methylene-bisacrylamide (20 μmol, 1.0ml of a 0.02 M solution in water) were added. The solution was then degassed for at least 4 hours before the reaction was heated at 65°C. After 12h, the viscous solution was cooled and dialyzed against deionized water for 3 days with water changed daily. The purified polymer was collected and evaporated under vacuum. The product was isolated with yields from 15 to 30 %.

Preparation of amine salts of monomer I. The monomer I (0.5g) was placed in a round bottom flask equipped with a temperature monitoring system. Methanol (5ml) was added and the solution was stirred at 0^oC for 5 min. A large excess of amine (3ml) was then added drop-wise. The reaction was stirred at room temperature for 2h and heated to 65^oC for 1h. After being cooled to room temperature, the methanol and un-reacted were evaporated under vacuum. The resulting compound was finally analyzed.   Butylamine ^{1}H, δ(d-DMSO): 0.86 (m, 3H, CH$_3$), 1.31 (m, 2H, CH$_2$), 1.51 (m, 2H, CH$_2$), 1.91 (s, 3H, CH$_3$), 2.79 (m, 2H, CH$_2$), 5.45 (m, 2H, CH$_2$), 5.84 (m, 1H, CH). Amylamine ^{1}H, δ(d-DMSO): 0.85 (t, 3H, CH$_3$), 1.26 (m, 4H, CH$_2$), 1.52 (m, 2H, CH$_2$), 1.90 (s, 3H, CH$_3$), 2.76 (m, 2H, CH$_2$), 5.42 (m, 2H, CH$_2$), 5.81 (m, 1H, CH).

Preparation of amine salts of 2-D polymer. The procedure was the same as described for the preparation of the amine salts of monomer I. Butylamine ^{1}H, δ(d-DMSO): 0.84 (t, 3H, CH$_3$), 1.29 (m, 2H, CH$_2$), 1.59 (m, 2H, CH$_2$), 2.5 (m, CH$_3$ + DMSO), 2.87 (m, 2H, CH2), 8-9 (br, NH). Amylamine ^{1}H, δ(d-DMSO): 0.83 (m, 3H, CH$_3$), 1.26 (m, 4H, CH$_2$), 1.63 (m, 2H, CH$_2$), 2.48 (m, CH$_3$ + DMSO), 2.84 (m, 2H, CH$_2$), 8-9 (br, NH).

Results and Discussion

The monomer I was prepared as described in the literature from the methacryloyl chloride and the 5-aminotetrazole with a 60 % yield (Aden, 2002) (Figure 7-1). The
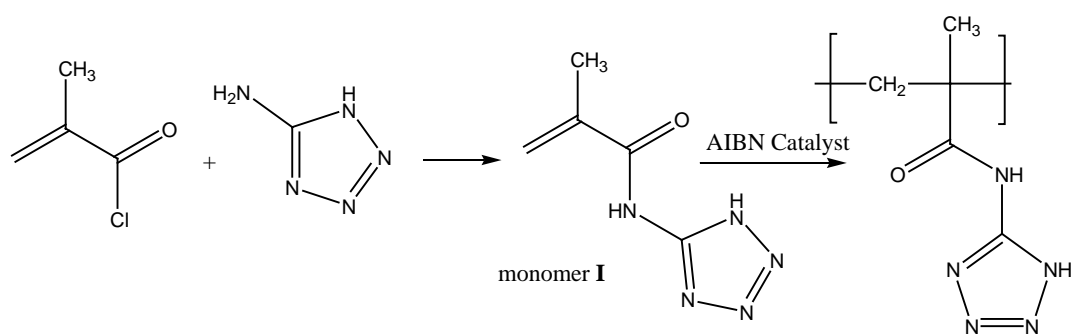
Figure 7-1.   General synthetic scheme for the preparation of the monomer **I** and its subsequent polymerization.

melting point of the white solid was 220.2^{o}C and occurred with decomposition. The reaction was then scaled up in order to have a sufficient amount of monomer for the polymerization step.

The polymerization was first attempted in the presence of 2,2'-azobisisobutyronitrile (AIBN) in dimethylformamide (DMF). The polymerization mechanism followed a radical pathway. Since oxygen interfered with the radical polymerizations, all the solvents were degassed before the reaction was engaged. The temperature was increased to 65°C in order to allow the reaction to take place. The first attempt was not as successful. The polymerization did occur, however the major products detected by NMR were the un-reacted starting materials. After examination, the solvent degassing was performed more thoroughly and the reaction was successful. The melting point was higher than 300 ^{o}C, which was the limit of the melting point apparatus. Regardless of the solvents and options used, no GPC spectrum was successfully recorded. This problem was caused by the extremely low solubility of the polymer in organic solvents and water. For the same reason, no NMR spectra in the liquid phase were of sufficient quality.

The DSC spectrum was then recorded for the 2-dimensional polymer. The exotherm was measured at 325 J/g which was notably lower than GAP (2100 J/g) and slightly lower than the tosyl substituted glycidyl tetrazole polymer (GTP) (797 J/g). The presence of the carbonyl was detrimental to the exotherm, however, other groups could be used in place of the carbonyl to increase the energetic potential (Cooper, 1983; Drain, 1963; Kepler, 1987; McBride, 1956; Ranganathan, 1994; Taylor, 1976).

Another series of experiments combined the chemistry of the gels with the principles of ionic liquids. For this approach, the polymerization was performed in the presence of a cross linker which induced the 3-D network formation (Figure 7-2). The experiment was attempted on the key monomer.

The cross linker—N,N-methylene-bisacrylamide—was chosen in accordance with the literature. The catalyst was therefore changed from AIBN to 2,2'-azobis(2-methylpropionamidine) dihydrochloride (V-50) because of water solubility. The monomer was first reacted with a base to make it water-soluble before the reaction was engaged at 65° C. The polymerization occurred as expected. The purification of the resulting polymer was performed using membrane filtration. The polymer was characterized by NMR and regardless of the conditions, the GPC did not produce conclusive results. The 2-D polymer was a white solid which exhibited almost no solubility in all the solvents tested. However, the 3-D polymer made a colorless film on the flask (Figure 7-3). It had a glassy appearance when removed from the flask. This observation demonstrated that the physical properties of these materials were dependent on the type of cross-linking network used in the synthesis.

As depicted in Figure 7-4, the monomer was reacted with the two amines that were the most successful in the synthesis of the simple tetrazole ionic liquids (e.g. butylamonium-5-methyltetrazolide and amylamonium-5-methyltetrazolide). In both cases, the reactions were carried out in methanol at room temperature, and were heated to 60^oC for 1h. The reaction was quantitative; the excess solvent and un-reacted amine were removed under vacuum. As always, the reactions were carefully kept under blast shields.
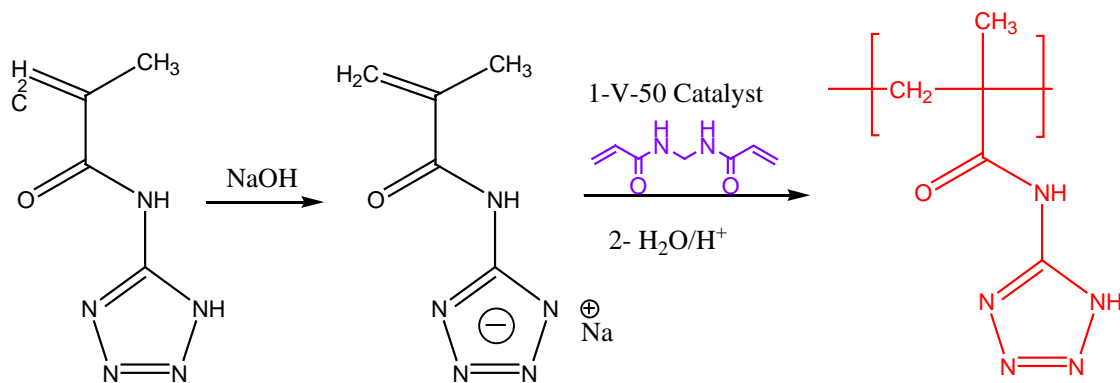
Figure 7-2.   General scheme for the preparation of 3-D polymeric network
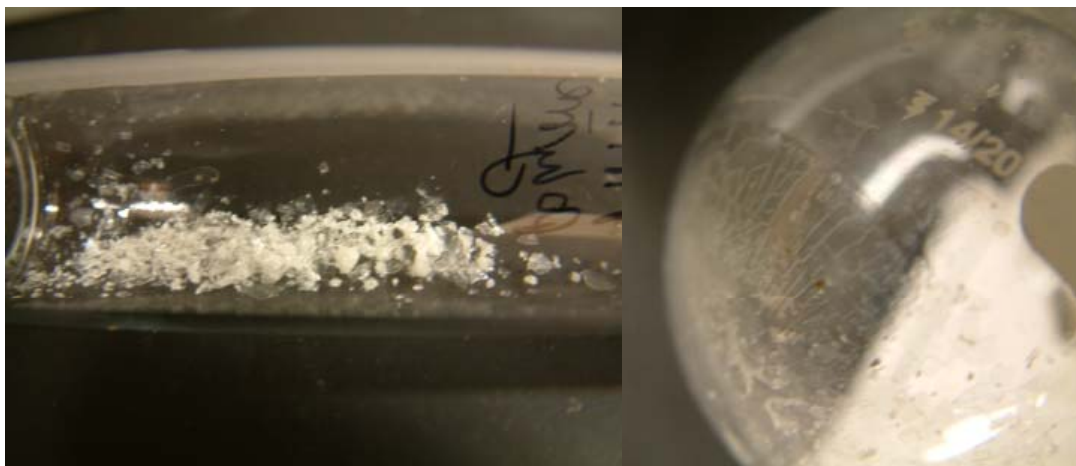

Figure 7-3.   Pictures of the 3-D polymers when on the flask wall as well
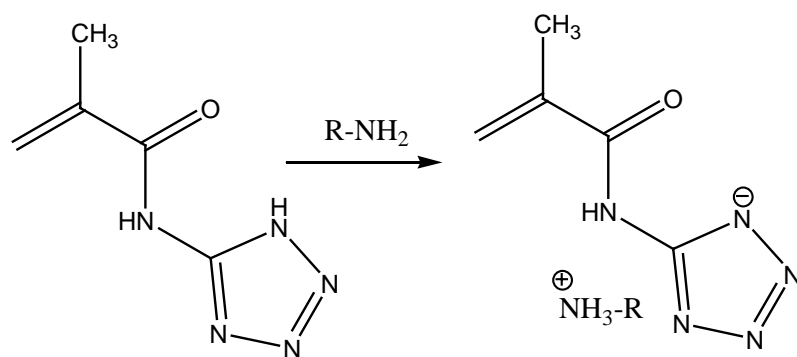   after collection into a vial.

Figure 7-4.   General scheme for the preparation of ionic species
from the neutral monomer.

When the butylamine was used as the base, the melting point of the ionic monomer (135.2^{o}C) was depressed by 85°C (compared to the non-ionic monomer melting point of 220.2^{o}C). In the case of the amylamine, the melting point depression observed from the monomer to the ionic form was 94.4^{o}C. The results of this experiment proved the critical role that this transformation played in tuning the physical properties of the final materials.

The next experiments involved repeating this process with the polymers rather than the monomers. The reaction went to completion in 1 hour in methanol at room temperature in the presence of an excess of amine. The completion of reaction was observed when all the insoluble starting materials present at the beginning of the reaction disappeared. The starting material polymer was insoluble but the ionic polymer produced was fully soluble in methanol. The products were analyzed by conventional liquid state NMR since the ionic polymer product was soluble in the deuterated solvents. When the butylamine was used, the ionic polymer exhibited a melting point of 206°C. When the amylamine was used, the ionic polymer exhibits a melting point of 211.6^{o}C. The melting point depression in both cases from the neutral polymer to the ionic polymer exceeded 100°C. This was a dramatic change that could be appropriately exploited to tune the physical and energetic characteristics of the polymer.

Conclusion

The results of these experiments proved that tetrazole gels can be synthesized and effectively tuned. Although the melting points were higher than expected, the data in this chapter illustrated the effects that small adjustments had on the physical properties of the energetic gels.

Perhaps the most important development from this work was the combination of the principles behind the energetic ionic liquids with the energetic gels. By combining these two technologies, a countless number of options were introduced. With further experimentation, these energetic gels could potentially satisfy the needs of any energetic application.

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CHAPTER VIII

RECOMMENDATIONS

Much of the work outlined in this thesis involved novel energetic materials. Therefore, some of the research was in a preliminary state. There were many recommendations and possibilities that involved combining the data and knowledge from each of these chapters. In this chapter, recommendations for each project will be suggested.

In Chapter II, the synthesis of 5-phenyl-1*H*-tetrazoles was discussed. The three major developments in this research were the protected tetrazole, the recyclable process, and the catalytic method. The primary recommendation would be to develop a method to combine these three advances. By adding the trityl chloride to a recyclable catalytic system rather than gaseous HCl, it should be possible to extract the product with little difficulty. With the aid of engineers, this process would not be difficult to implement.

In addition, these techniques should be used to make tetrazoles other than the 5-phenyl derivative. Toluene could serve as an adequate replacement for benzonitrile (Koguro, 1998). With this change, other nitriles could be added to the reaction. Although some of the efficiency of the reaction would be lost (because the solvent would no longer serve as the reactant), the overall process would surely be a success. There is little doubt that this process would safely and efficiently produce a wide array of 5-substitued tetrazoles.

In Chapters III and IV, the synthesis of a new series of glycidyl tetrazole polymers was outlined. As mentioned in Chapter IV, the first experiments attempted to replace the chlorine on the epichlorohydrin with a nitrile. If this reaction was successful,

the knowledge from Chapter II could be used to introduce a tetrazole on the side chain while avoiding the use of glycidyl azide polymer throughout the entire procedure. The attempt to replace the chlorine was a failure. The alpha hydrogens were likely extracted by the basic nitrile. Therefore, the primary recommendation for these chapters would be to design a synthetic step that would allow for an easy substitution of the chlorine. While at this time there are no specific suggestions, this would be an important development. With a nitrile-substituted polymer, the tetrazole could be safely synthesized. This procedure would also produce a tetrazole attached to the sidechain via the carbon in the ring. Compared to the isomer synthesized in Chapter IV, this polymer might possess a much higher energetic potential.

Beyond synthesizing the nitrile-substituted polymer, the only other recommendation involves the improvement of the overall process that utilizes the cyanoformates. The long reaction times hinder the progress of the project—especially considering the small quantities synthesized due to safety concerns. The ethyl and benzyl cyanoformates are also fairly expensive. If an easier route to the H-GTP was discovered, the speed of this research would significantly increase.

The energetic foams discussed in Chapter V would consume an entire thesis if all of the tunable avenues were explored. Currently, the main suggestion would be to synthesize a foam using a liquid glycidyl tetrazole polymer. While the pure GTP is a solid when the MW is 2000, the material should be a liquid at a higher molecular weight. This liquid material should be used to generate an energetic foam. The resulting foam would be a stable energetic structural framework that could be used in any of the
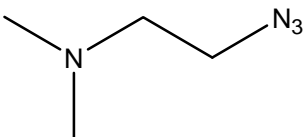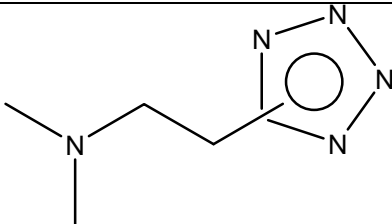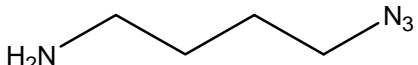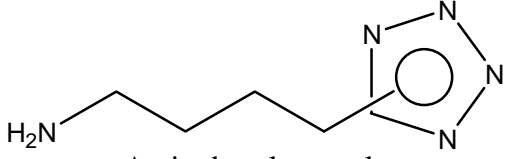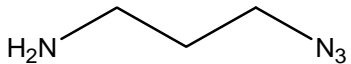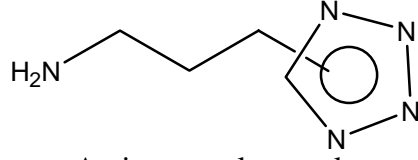
applications discussed in Chapter V. Without the presence of the azide groups, however, the foam would be safer and have a longer shelf life.

Like the energetic foams, the ionic liquids in Chapter VI created an endless number of potential experiments. One of the most significant possibilities involved the introduction of an energetic amine counter-cation. The ionic liquids were composed of an energetic component and a non-energetic component—the tetrazolide ring and the substituted ammonium, respectively. The research in Chapter V proved that the amine had a negative effect on the energetic potential of the molecule. The ionic liquids in which the substituted ammonium possessed a longer alkyl chain lowered the ratio of energetic to non-energetic components. The exotherm values clearly reflected the lost of energy. The ammonium counter-cation played a critical role in determining both the physical properties and the energetic potential of the ionic liquids.

To overcome the lack of energetic character in common amines, the design of an energetic counter-amine is recommended. Through literature searches, theoretical calculations, and discussions during meetings and workshops, the most promising candidates are those illustrated in Table 8-1. However, a careful balance between the energy intake and the alkyl chain length must be considered in order to maintain liquids properties yet increase the energy.

At the top of the list of potential amines is dimethylaminoethylazide (DMAZ). The synthesis of DMAZ is well known in the propellant field but is seldom reported in the literature (Green, 2004; McQuaid, 2003; Striebich, 2003, Miksa, 2003; Thompson, 2000). Others energetic amines are also summarized in Table 8-1.

Table 8-1. Energetic azido-amines and tetrazole base amines.

AZIDE AMINE DERIVATIVES	TETRAZOLE AMINE DERIVATIVES
Dimethylaminoethylazide (DMAZ)	Dimethylaminoethyltetrazole
Aminobutylazide	Aminobutultetrazole
Aminopropylazide	Aminopropyltetrazole

With the exception of DMAZ, the azide derivatives have been well described and the syntheses reported (Lee, 2001). The general scheme is outlined in Figure 8-1. The tetrazole-amines derivatives are novel compounds and their syntheses should be investigated. A synthesis for the tetrazole amines is shown in Figure 8-2. This scheme can also be applied to longer alkyl chains like aminobutyltetrazole. The synthesis is straightforward and the chemistry is well known. A number of tetrazole-amines can be prepared in three steps (Figure 8-2). The synthetic schemes allow the tetrazole to be attached either on the –N in 1 position or on the –C in 5 position.

The synthetic schemes, as observed, include a pathway to prepare DMAZ. The literature provides only one procedure to specifically prepare DMAZ (Schiemenz, 1959). This synthesis was conducted twice during the ionic liquids research, but unfortunately was unsuccessful. The major concern in this synthesis is safety, which raises the overall difficulty of this process. In addition, high dilution and the use of water as the solvent make the isolation difficult.

The energetic amines designed above are extremely promising in terms of energy intake according to the theoretical calculations currently under review. However, the experimentation will be critical in order to know the physical properties of their 5-methyltetrazole salts. The syntheses of the energetic amines are relatively straightforward. The major drawback is the concern about safety.

The last series of recommendations involves the energetic gels in Chapter VI. Although the energy potential of the gels will primarily come from the compounds entrapped in the matrix, the energetic properties of the monomer are an important consideration.
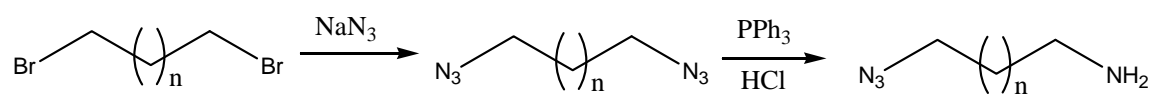
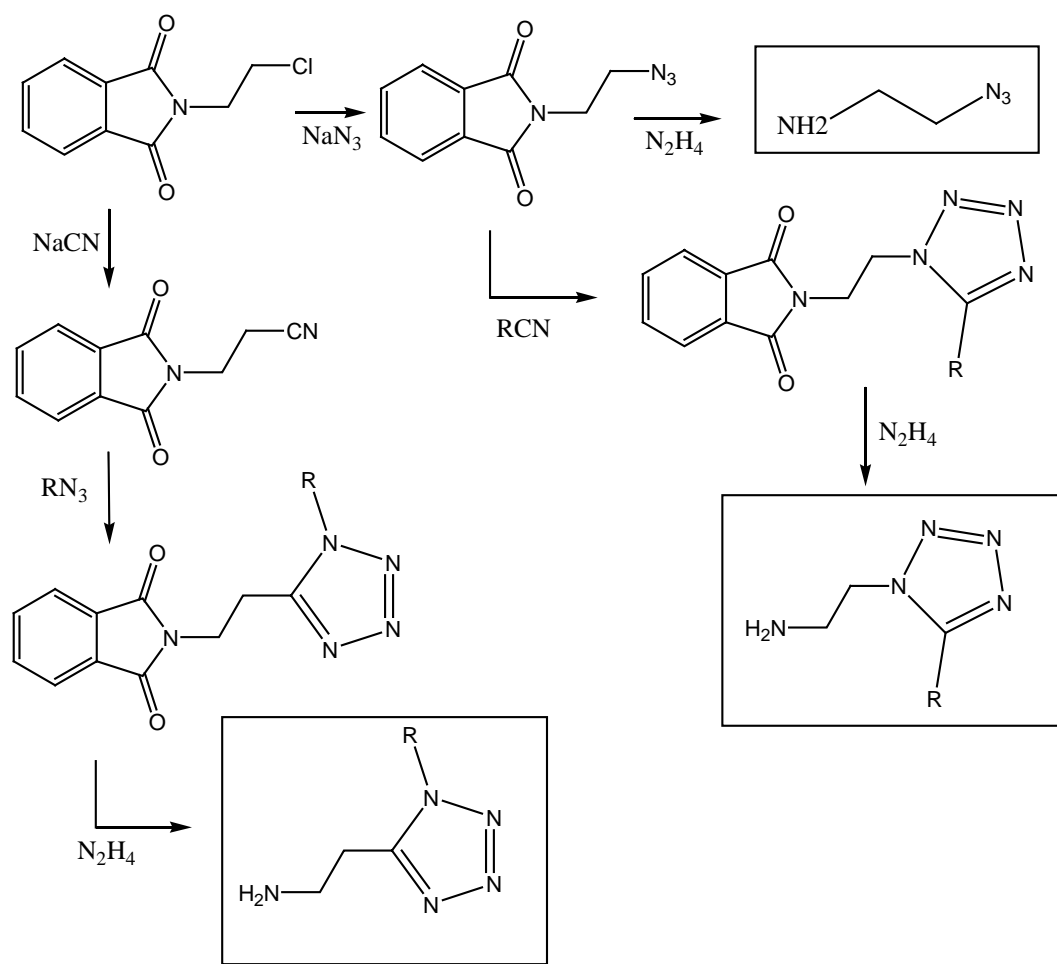Figure 8-1. Synthetic scheme to prepare long alkyl chain azido-amines

Figure 8-2. Synthetic scheme to prepare DMAZ, 5-alkylaminetetrazole and 1-alkylaminetetrazole. In this illustration ethylaminotetrazole are depicted.

Based on discussions held at meetings and energetic workshops, it is believed that the carbonyl and the methyl groups are responsible for the mediocre exotherm values observed in Chapter VI. A structure modification will consequently be needed in order to enhance the final performance. The methyl group is needed to allow good yields during the monomer synthesis—and should remain unchanged. However, the carbonyl is detrimental in terms of energy potential so it should be modified into groups that will strongly contribute to the overall energy (Figure 8-3). Several groups should be considered to counter this problem (Cooper, 1983; Drain, 1963; Kepler, 1987; McBride, 1956; Ranganathan, 1994; Taylor, 1996). By calculating their theoretical potential, specific experiments will enhance the energetic properties of the molecules.

With these recommendations, the performance of each molecule in this thesis could be improved. There are literally thousands of possibilities with regard to foams, gels, and ionic liquids that could be implemented and studied. Great strides have been made; and these suggestions will only enhance all of these projects.
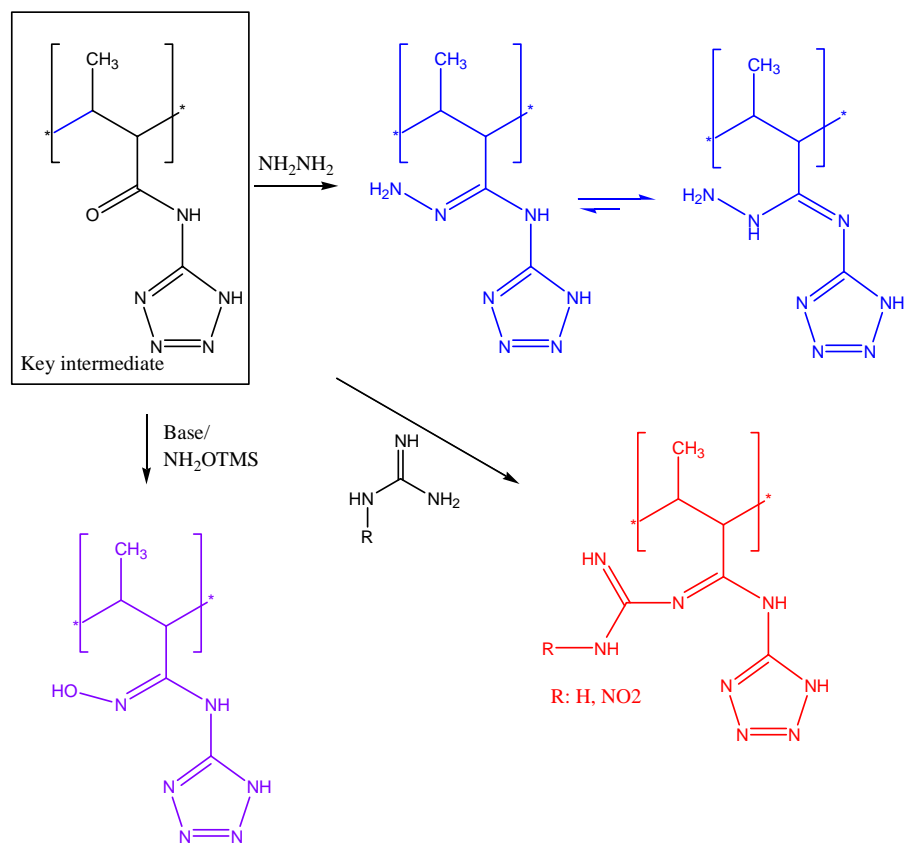
Figure 8-3. Synthesis pathways to prepare novel and enhance energetic polymers.

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