ENERGETIC POLYMERS

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in
Chemistry
Under the Faculty of Science

by

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Under the Supervision of

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Certificate

*This is to certify that the thesis entitled "**Energetic Polymers**" submitted for the award of the Degree of Doctor of Philosophy of the Cochin University of Science and Technology, is a record of original research work carried out by Mr. Anoop. N. A under my supervision and guidance in the Department of Applied Chemistry and further that it has not formed the part of any other thesis previously.*

Kochi – 22
12th September 2013

Dr. K. Sreekumar
(Supervising Teacher)

Declaration

*I hereby declare that the thesis entitled "**Energetic Polymers**" submitted for the award of Ph.D. Degree of the Cochin University of Science and Technology, is based on original research work done by me under the guidance of Dr. K. Sreekumar, Professor, Department of Applied Chemistry, Cochin University of Science and Technology and further that it has not previously formed the basis for the award of any other degree.*

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12th September 2013

Anoop. N. A

"God, our Creator, has stored within our minds and personalities, great potential strength and ability. Prayer helps us tap and develop these powers. Look at the sky. We are not alone. The whole universe is friendly to us and conspires only to give the best to those who dream and work."

A.P. J. Abdul Kalam

Dedicated to my Family

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Above all I bow my head to almighty who gave me strength to cross the toughest situations.

Anoop N A

Preface

High energy materials are essential ingredients in both rocket and explosive formulations. These can be vulnerable due to maltreatment. During gulf war, several catastrophic accidents have been reported from their own payload munitions. The role of energetic binders here was to wrap the explosive formulations to convert it into insensitive munitions. With the aid of energetic binders, the explosive charges are not only protected from tragic accidents due to fire, bullet impact, adjacent detonation, unplanned transportation, but also form total energy output presumption.

The use of energetic binders in rocket propellants and explosive charges has been increased after the Second World War. Inert binders in combination with energetic materials, performed well as binders but they diluted the final formulation. Obviously the total energy output was reduced. Currently, the research in the field of energetic polymers is an emerging area, since it plays crucial role in insensitive munitions.

The present work emphasises on the synthesis and characterization of oxetanes, oxiranes and polyphosphazene based energetic polymers. The thesis is structured into six chapters. First part of chapter 1 deals with brief history of energetic polymers. The second part describes a brief literature survey of energetic polymers based on oxetanes and oxiranes. Third and fourth parts deal with energetic plasticizers and energetic polyphosphazenes. Finally, the fifth part deals with the various characterization techniques adopted for the current study and sixth part includes objectives of the present work.

Second chapter includes the synthesis and characterization of oxetane based energetic polymers. It includes the synthesis of PECH-THF diol and its characterization, followed by the synthesis and characterization of GAP-THF diols, poly(dinitropropanoxy) oxirane (PDNPO) and poly(bistrifluroethoxy) oxirane (PBTEO).

Third chapter emphasises on the synthesis and characterization of copolymers of both oxetanes and oxiranes. Here three copolymers such as BAMO-GLYN copolymer, BAMO-NMMO copolymer and GAP-BAMO copolymer are synthesized and characterized.

Fourth chapter deals with the synthesis and characterization of novel energetic polyphosphazenes. First section in this chapter includes the synthesis of polydichlorophosphazene and in the second part, the attachment of energetic moiety of both aliphatic and aromatic nature are discussed.

Fifth chapter focuses on the binder properties of the synthesized polymers. The binder properties such as heat of formation, glass transition temperature, molecular weight and oxygen balance are evaluated and discussed. Characterization of the polymers was carried out with ^{1}H, ^{13}C, ^{31}P *NMR, IR spectroscopy, GPC, DSC and bomb calorimeter.*

In the final chapter, the summary of the investigations, conclusions drawn from the earlier chapters and future outlook are presented.

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Chapter 1

INTRODUCTION AND LITERATURE SURVEY

1. Introduction

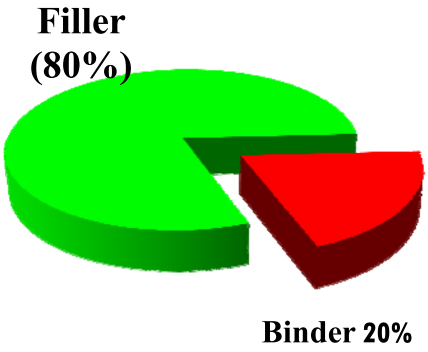
Several catastrophic accidents have been reported in connection with stored explosives due to fire, bullet impact, adjacent detonation, unplanned transportation etc. Adopting important design considerations such as extended service life, decreased signature, enhanced mechanical properties, low environmental effect etc. could reduce such accidents. One strategy to overcome these problems is the use of cast cured polymer bonded explosives (PBX) [1]. In PBX, explosives are suspended in a polymeric binder and which cured in situ to form a tough elastomeric rubber which is capable of absorbing and dispersing energy from explosive formulation. The polymeric binder used to bind the explosive formulations which cured in situ with the help of a curing agent to form a tough three dimensional network.

In past days, mixture of nitrocellulose and nitroglycerine was used as binder for energetic ingredients, in which nitrocellulose was used to thicken nitroglycerine and to reduce the impact, friction sensitivity. After demilitarization it was difficult to recover and recycle these binders [2].

While using hydroxyl terminated polybutadiene (HTPB), explosives are encapsulated in the binder and crosslinked with isocyanates, containing plasticizers such as dioctyl adipate (DOA). Carboxyl terminated polybutadiene (CTPB) and hydroxyl terminated polyethers (HTPE) are polymers of the same category and these binders exhibit excellent physical properties and reduce the vulnerability of explosive charges [3]. Inert binder systems have been employed effectively in explosive compositions for underwater and air-blast application, but it is difficult to formulate high performance cast-cured explosives for metal acceleration. One strategy is to change the fabrication method from cast-cure to twin screw extrusion or injection moulding, thereby reducing the quantity of inert binder required. Another approach has been to use polymers and/or plasticizers which contribute to the overall energy of the composition. This has led to the development of high performance explosives and advanced rocket propellants.

Conventional binder system consists of fuel (5-22% powdered Aluminium, Magnesium, Berylium, RDX, CL-20, HMX etc., oxidizer (65-70% Ammonium perchlorate (NH_4ClO_4); Ammonium nitrate (NH_4NO_3) etc., and binder (8-14% hydroxyl terminated polybutadiene (HTPB) along with plasticizer [4]. The following represents the composition of conventional polymer bonded explosives (PBX). The advantage of the energetic binder systems over conventional binder system is that we can reduce the amount of crystalline fillers without affecting the overall energy output of the formulation.

Conventional Binder System



Eneregetic Binder System

Plasticizers are used in energetic binder systems for PBXs to fulfill a number of requirements including [5]:

- Lowering the viscosity to improve processing,
- Lowering the Tg (glass transition temperature) to improve mechanical properties.
- Altering the explosive performance of the PBX, and
- To improve safety of the PBX.

Most plasticizers that find use in PBXs commonly display exudation from the binder matrix even under storage conditions. This is highly undesirable since degradation of mechanical and IM properties may result [6]. It is well known that if the plasticizer closely resembles the PBX polymer, exudation can be lowered or reduced markedly.

Conventionally used energetic polymer binders such as polyBAMO, polyNMMO, polyGLYN etc may be used in conjugation with high explosives such that the energy of the explosive itself is not overlay diminished by the presence of binder in the combined material [7]. The difficulty with this approach is in obtaining energetic polymers, which when used as binders have an adequate combination of both desirable physical properties such as malleability and shock insensitivity, in addition to high energy density. Even the best energetic binders have energy densities that are significantly lower than that of the crystalline explosive material for which they are required to bind. This has the effect of reducing the energetic performance of the explosives. In an attempt to solve this problem, current practice is to use a high loading of explosive relative to binder which in turn diminishes the desirable physical properties of the binder/explosive mixture. Energetic binders based on polypohsphazenes have low glass transition temperatures without the need for plasticization, to avoid rigidity at low temperatures. Since some of the polyphosphazenes are miscible with other energetic polymers (eg: polyNMMO, polyGLYN), it is possible to construct a chemically cured system comprising a mixture of polyphosphazene with these binders (i.e. by using the polyphosphazene as co-binder using traditional curing technology).

Modern energetic binders consisting of energetic polymer and plasticizers need more energy content, but at the same time this should be more insensitive to comply with insensitive munitions criteria. The characterization of these energetic polymers is of importance to explosive chemists; knowledge and understanding of density, velocity of detonation, stability and compatibility, burning characteristics, degradation chemistry, side reactions and polymer morphology are all essential. Further aspects to be addressed are safety, suitability for service and useful service life [8].

The next generation of energetic binders therefore require precise characterization by analytical techniques to determine molecular weight, molecular weight distributions and functionality (amount of reactive functional groups per molecule), to allow optimization of the curing process. Binder systems typically consist of a polymeric binder with plasticzer(s), which act to improve processability and the mechanical properties of the PBX.

2. History of Energetic Polymers

2.1 Polysulfide

Ever since the introduction of nitrocellulose (NC) as an explosive fill in the 1850's, polymers have contributed considerably to advancements in the technology of both propellants and explosives. In addition to the specific instance of the use of NC polymer in explosive fills, applications of polymers have been most extensive in binders and plasticizers. Over the years, with the maturity of composite propellant and polymer bonded explosive technology, diverse classes of polymers have been developed for binder applications, in order to meet the dual objectives of insensitivity and high performance.

Polysulfide (Fig.1) was the first polymer to be used as a binder in the heterogeneous (composite) family of propellants in 1942 [9]. It was invented by Dr. Joseph C. Patrick in 1928 as a condensation product of ethylene dichloride with sodium polysulfide. He named this polymer Thiokol and formed the Thiokol Corporation to commercialize the product. The sulphur in the polymer backbone functioned as an oxidizer in the combustion process contributing towards higher specific impulses. The polymer could be cross-linked by oxidative coupling with curatives such as p-benzoquinone or manganese dioxide to form disulfide (–S–S–) bonds. The cured elastomers have good elongation properties for wider operating temperature ranges.

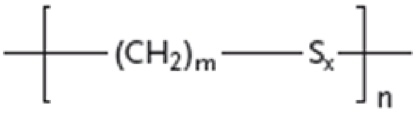


Figure 1: Polysulfide

2.2 Polybutadienes (PBAA, PBAN, and CTPB)

In early 1955, the role of aluminum as a high performance ingredient in propellant formulations was demonstrated by Charles B. Henderson's group at the Atlantic Research Corporation, USA. The polysulfide propellant developed by Thiokol could not be adapted to the use of aluminum, because chemical reactions during storage led to explosions. Therefore a new series of binders based on butadienes were developed by Thiokol. Furthermore, a polybutadiene chain polymer was found to be more favorable than a polysulfide chain to provide higher elasticity [10]. The first of the butadiene polymers to be used in a propellant was the liquid copolymer of butadiene and acrylic acid, PBAA (Figure 2) developed in 1954 in Huntsville, Alabama, USA. The PBAA was prepared by the emulsion radical copolymerization of butadiene and acrylic acid. However, owing to the method of preparation, the functional groups are distributed randomly over the chain. Hence, propellants prepared with PBAA show poor reproducibility of mechanical properties [11].

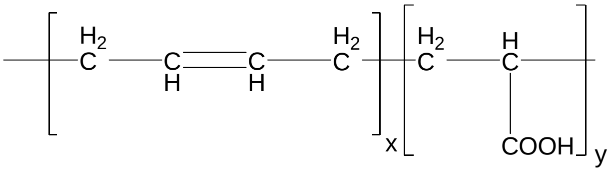


Figure 2: PBAA

The mechanical behaviour and storage characteristics of butadiene polymers were improved by using terpolymers based on butadiene, acrylonitrile, and acrylic acid (PBAN) (Figure 3) developed by Thiokol in 1954. The introduction of an acrylonitrile group improved the spacing of the carboxyl species. This polymer has low viscosity and low production costs.

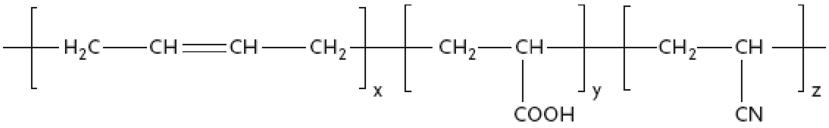


Figure 3: PBAN

In late 1950s, carboxyl terminated polybutadiene (CTPB) (Figure 4) with the trade name HC-434, which took full advantage of the entire length of the polymer chain, was developed by Thiokol [12].

HC-434 was prepared by the free-radical polymerization using azo-biscyanopentanoic acid initiator. In parallel to the Thiokol polymer work, Phillips Petroleum Company developed another brand of CTPB known as Butarez CTL, which was prepared by lithium initiated anionic polymerization. CTPB propellants offer significantly better mechanical properties particularly at lower temperatures in preference to PBAA or PBAN binders, without affecting the specific impulse, density, or solid loading [13]. The curatives for CTPB prepolymers are the same as that for PBAA and PBAN. CTPB formulations were used in propellants from the 1960s. In 1966, the CTPB based propellant TP-H-3062 was used in the surveyor retro motor for the first landing on the moon.

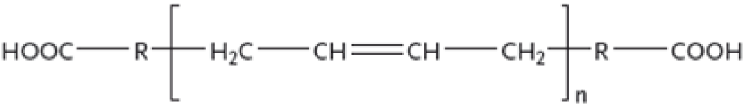


Figure 4: CTPB

2.3 Polyurethanes

Almost concurrently with the development of polybutadiene polymers, Aerojet, who were a competitor to Thiokol, developed the polyurethane branch of binders, in the mid-1950s. Polyurethane binder, the general structure of which is shown in Figure 5 is formed by the reaction of a high molecular weight difunctional glycol with a diisocyanate forming a urethane linked polymer. Polyurethane binder systems provide shrink-free, low-temperature, and clean cure.

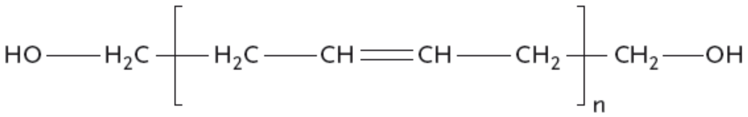
An additional benefit of polyurethane binder is that, the backbone polymer contains substantial amount of oxygen [14]. It is not necessary, therefore, to use a high percentage of oxidizer in the formulation of the propellant to achieve comparable energies. Also, several of the urethane polymers are known for their thermal stability.

$$-\!\!\left[R - NH - COO - R' \right]_n\!\!-$$

Figure 5: Polyurethane

2.4 Hydroxyl Terminated Polybutadiene

The applicability of hydroxyl terminated polybutadiene (HTPB) polymer as a binder was demonstrated by Karl Klager of Aerojet in 1961 [15]. HTPB (Figure 6) was prepared by the free radical polymerization of butadiene using hydrogen peroxide as the initiator. Even though the development of HTPB began in 1961, it was not proposed to NASA until 1969 due to the popularity of PBAN and CTPB formulations. HTPB binder was first tested in a rocket motor only in 1972 [16]. It was commercialized with the trade name R-45M by ARCO chemical's. Isocyanates are used as crosslinking agents for HTPB polymers to form urethane linkages, thereby reuniting the polyurethane family of binders with the polybutadiene family. HTPB binders exhibit superior elongation capacity at low temperature and better ageing properties over CTPB [17]. It has since become the most widely-used binder in solid propellant formulations with excellent mechanical properties and enhanced insensitive munition (IM) characteristics.



$HO-H_2C-[H_2C-CH=CH-CH_2]_n-CH_2-OH$

Figure 6: Hydroxyl Terminated Polybutadiene

2.5 Thermoplastic Elastomers

In the early 1980s, screw extrusion technology was envisaged for processing of energetic material formulations, particularly PBX, with the core objective of reducing the cost of production [18]. For its effective implementation, thermoplastic elastomers (TPE) began to be used as binders. TPEs consist of alternate hard and soft segments of crystalline and amorphous polymers, possessing the combined properties of glassy or semi-crystalline thermoplastics and soft elastomers. TPE technology enabled rubbers to be processed as thermoplastic. Block copolymers of styrene and ethylene/butylene (Kraton G-6500) are widely used as binders in a variety of energetic material formulations including rocket propellants, explosives, and pyrotechnics. Kraton G-6500 (Figure 7) is a triblock copolymer of styrene–ethylene/ butylene–styrene (SEBS) prepared by anionic polymerization using alkyl lithium initiators.

The polystyrene block is the hard segment and the polyethylene/butylene block constitutes the soft segment. At room temperature, the flexible rubbery polyethylene/ butylene blocks (Tg ~ -100 ^{0}C) are anchored on both sides by the glassy polystyrene blocks (Tg ~ 100 ^{0}C). Therefore, they behave as crosslinked rubber at ambient temperature and allow thermoplastic processing at higher temperatures [19].

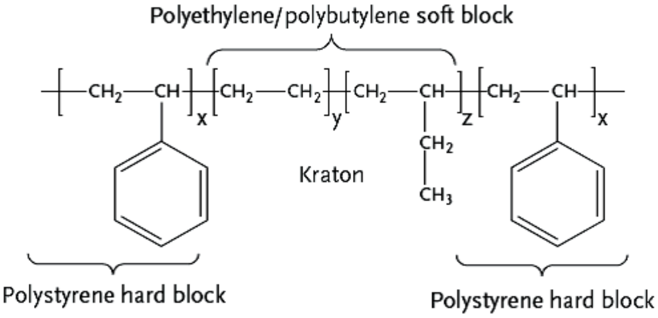


Figure 7: Thermoplastic Elastomers

3. Energetic Polymers

Above said binder systems have excellent physical properties and reduce the vulnerability of explosive charges, but they are inert, i.e., the binder dilutes the explosive, reducing the overall energy output and the performance of the composition. One strategy is to change the fabrication method from cast-cure to extrusion or pressing, thereby reducing the quantity of inert binder required. Another approach has been to use polymers and/or plasticzers which contribute to the overall energy of the composition. This has been successful in the development of high performance explosives and advanced rocket propellants. A more radical approach is inclusion of energetic functional groups, such as azido, nitro (C-nitro, O-nitro (nitrate esters) and N-nitro (nitramines)) and difluoramine groups, along the polymer backbone and in the plasticzer. Incorporation of these explosophores increases the internal energy of the formulation, in addition to improving the overall oxygen balance.

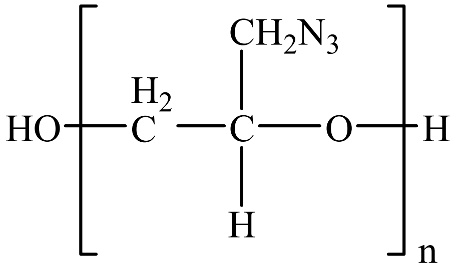
New energetic binders [20] that appear to offer such promise include azide functional polymers like glycidyl azide polymer (GAP), or the nitrato polyethers like poly(3- nitratomethyl-3-methyl) oxetane (polyNMMO), and poly(glycidyl nitrate) (polyGLYN). [Monomers are NMMO, 3-nitratomethyl-3-methyloxetane and GLYN, glycidyl nitrate, respectively] etc. Energetic plasticizers include oligomers of the polymers mentioned above, as well as a wide variety of nitrate esters, nitroaromatics and azido plasticizers.

3.1 Oxirane Polymers

3.1.1 Glycidyl Azide Polymers

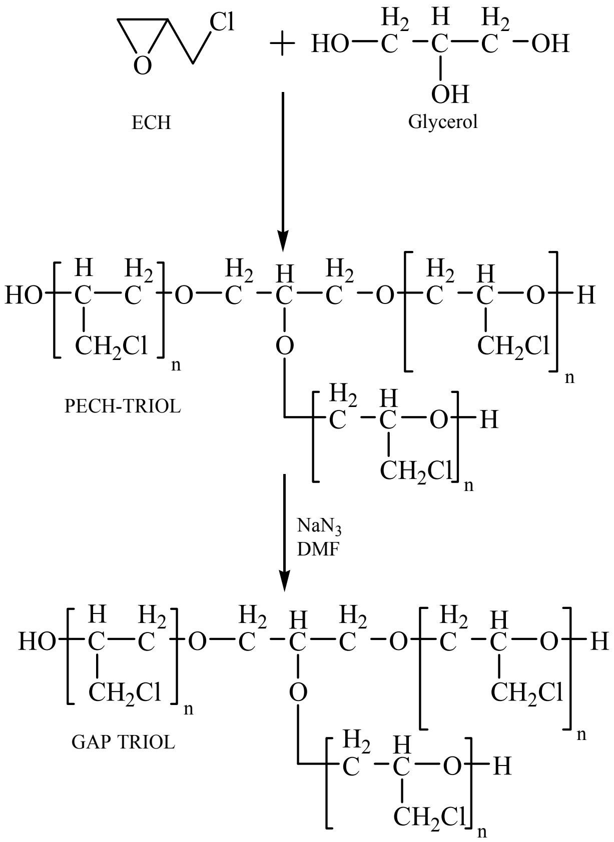
Azido functionalised polymers such as glycidyl azide polymer (GAP) were reported as heralding the next generation of energetic binders early in the 1980s [21]. The safety characteristics of GAP loaded with RDX (RDX/GAP 86.4/13.6) are almost the same as those for RDX compositions made with the inert HTPB binder (RDX/HTPB 86.4/13.6) [22]. Glycidyl azide polymer can be used as an energetic binder (at MW 2000-6000) in composite explosives and solid rocket propellant systems to impart additional energy to the formulations which increase the performance and enhance the stability and the mechanical properties of the system.

GAP was first synthesized in 1972 by Vandenburg [23] by the reaction of sodium azide in dimethylformamide with polyepichlorohydrin, PECH-triol. Frankel and coworkers at Rocketdyne [24] synthesized PECH-triol by polymerization of epichlorohydrin (ECH) with glycerol as the initiator unit, as shown in Figure 8. GAP may be crosslinked by reaction with isocyanates to give an extended polymeric matrix.



$$HO\left[-\overset{H_2}{C}-\underset{H}{\overset{CH_2N_3}{C}}-O-\right]_n H$$

Figure 8: GAP



Scheme 1: Synthesis of GAP Triol

This general process can also be used to produce linear GAP-diol and branched GAP diol polymers [25,26]. The first step of the process can actually be by-passed, as commercial quantities of PECH-diol are available. Optimization of PECH production has led to the successful development of a process which yields GAP polymers having average molecular weights of 2100 and functionalities (the number of reactive hydroxyl groups per molecule) of 1.6 to 3.1, depending on the catalyst, the initiator and the ratio of ECH/initiator. The azidation step can now be carried out in aqueous solvent or organic solvent or in polyethylene oxide [27]. The functionality of linear GAP is nearly 2, and to achieve the desired level of crosslinking to produce a tough and elastomeric rubber, it must be raised by the addition of triols or used with triisocyanate crosslinkers [28].

3.1.1.1 GAP Properties

The physico-chemical properties of GAP depend on the degree of polymerization, structure and method of preparation.

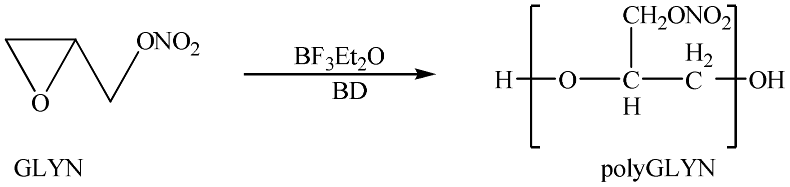
Table 1: GAP Diol and Triol Polymers [29]

	GAP Diol	**GAP Triol**
Density, g/cm^3	1.29	1.29
Colour	Light yellow liquid	Light yellow liquid
Heat of Formation, ΔH_f, cal/g	280	280
Mn	1700 ±300	≥900
Functionality	2.0	2.5-3.0
Vacuum stability,mL/g,200h,100^{0}C	≥3	≥3
Tg,^{0}C	-45	-45

The energetic properties of GAP are not a consequence of its oxidation products, but rather are due to chain scission of the azide group, which gives nitrogen gas with a heat of reaction of + 957 kJ/kg at 5 MPa [30,31]. GAP also contains a relatively high concentration of carbon atoms, and therefore has a high combustion potential [32], burning smoothly at elevated temperatures and pressure (>0.3 MPa) without explosion [33]. Thermal decomposition studies have been widely examined for GAP. Differential thermal analysis and thermogravimetric studies (DTA/TGA) of the decomposition of GAP under a helium atmosphere (0.1 MPa) revealed an exothermic decomposition at 202-277°C accompanied by a 40% weight loss, followed by a secondary weight loss without heat liberation [34].

3.1.2 PolyGLYN

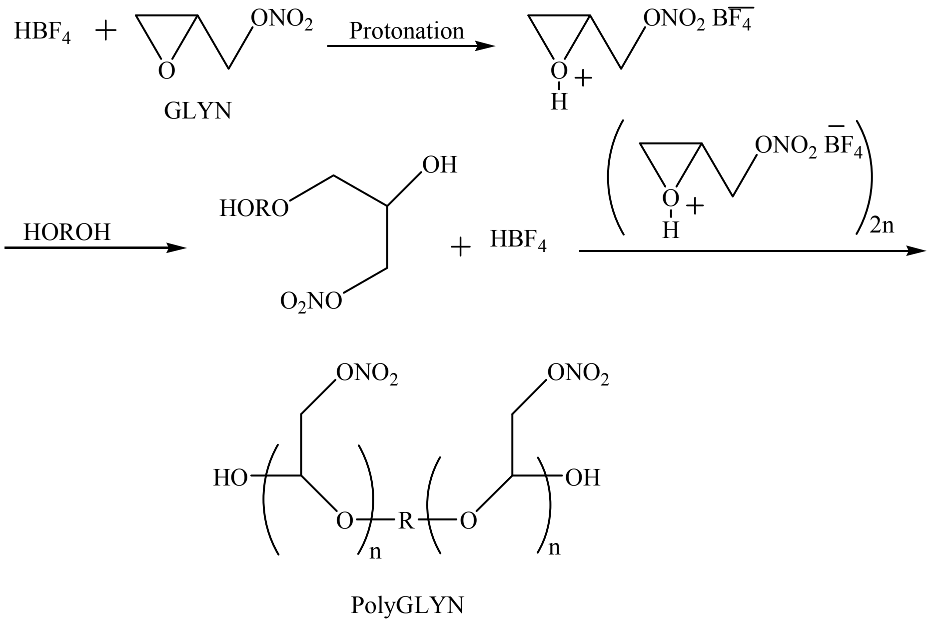
Poly(glycidyl nitrate) (PGN) has been known and recognized as a possible energetic polymer suitable for use in propellants, explosives [35], gas generants, pyrotechnics, and the like. PGN is most commonly synthesized in the industry by a three-step procedure characterized by a first step in which epichlorohydrin is nitrated, and a second step in which the nitrated epichlorohydrin is recyclized with a base to form glycidyl nitrate [36]. The glycidyl nitrate is then polymerized in a third step by cationic polymerization to form PGN. The selection of epichlorohydrin derives from the low cost of the reagent and the relatively high nitration yields obtained by the nitration of epichlorohydrin. Despite these relatively high nitration yields, in the subsequent recyclization step an appreciable amount of epichlorohydrin is regenerated with the glycidyl nitrate. The presence of epichiorohydrin during subsequent cationic polymerization is highly disadvantageous, since the epichlorohydrin, unless removed, will copolymerize with the glycidyl nitrate to decrease the nitro group concentration of the resulting copolymer [37,38].



Scheme 2: Synthesis of polyGLYN

PGN may be used in combination with conventional or novel propellant and solid explosive ingredients as the basis for formulating very high performance insensitive propellant and explosive compositions. Representative explosive materials that can be made with PGN, as the sole binder or one of a plurality of binders, include gun propellants, cast cure explosives, and extruable explosives[39].

GLYN, like its oxetane counterpart NMMO, is now prepared using N_2O_5 [40] in a flow reactor to give dichloromethane solutions in high yields and high purity, requiring no further purification before polymerisation. Polymerisation of the prepolymer employs a tetrafluoroboric acid etherate initiator (not boron trifluoride etherate initiator, as used in the synthesis of polyNMMO) combined with a di-functional alcohol (glycol), to give a nominally di-functional polymer. Slow addition of the monomer solution to the initiator solution generates an activated monomer unit, which combines with the alcohol in a ring opening process, regenerating a proton. The proton activates a further monomer unit, which adds to the polymer chain. Reaction is terminated by quenching in excess water followed by neutralisation [41]. The active monomer polymerization of GLYN is given in scheme 3.



Scheme 3: Active Monomer Polymerization of GLYN

3.1.2.1 Properties of PolyGLYN Prepolymer

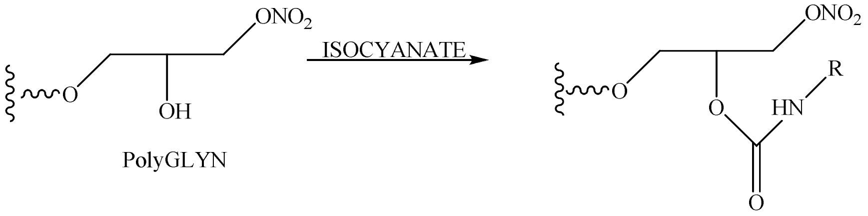
PolyGLYN prepolymer is a clear, yellow liquid high in energy and density with a low Tg (Table 2). In addition, its sensitiveness is classed as too low to require classification as a Class 1 explosive. PolyGLYN has a calculated energy of 2661 kJ kg^{-1}, comparatively higher than both GAP and polyNMMO (2500 and 818 kJ kg^{-1}, respectively) [42].

Table 2: Typical Properties of Poly(GLYN)

PolyGLYN	
Density, g/cm^3	1.46
Tg, ^{0}C	-35
Heat of formation, Kcal/mol	-68
Functionality	~2
Hydroxy value (mg KOH/g)	~37
O_2 balance	-60.5

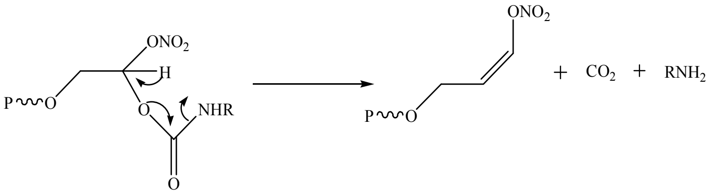
3.1.2.2 Stability of PolyGLYN Rubber

Uncured polyGLYN prepolymer (scheme 4) exhibits good chemical stability. However, when cured with isocyanates the resulting polyurethane rubbers show poor stability [43].



Scheme 4: Uncured and Cured PolyGLYN

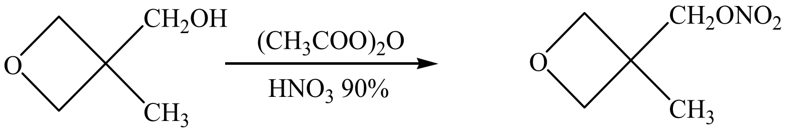
Further, degradation is not prevented by the presence of stabilisers, or by the exclusion of oxygen. This decomposition of polyGLYN rubber (scheme 5) is attributed to a low activation energy degradation associated with chain scission at the urethane linkage and has little to do with the normal nitrate ester degradation process [44]. Such chain scission is not possible in the case of polyNMMO, which has no labile H atom available for transfer.



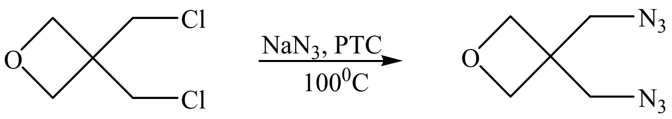
Scheme 5: Chain scission of cured polyGLYN

3.2 Oxetane Polymers

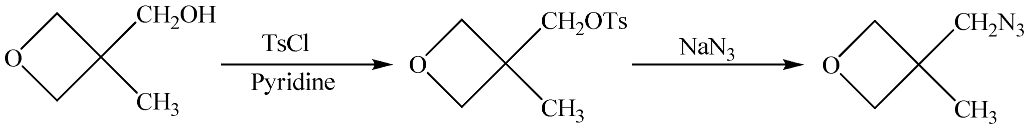
Energetic polyoxetanes were first synthesised by Manser from monomers such as 3-nitratomethyl-3-methyl oxetane (NMMO), 3,3-bis-(azidomethyl)oxetane (BAMO) and 3-azidomethyl-3-methyl oxetane (AMMO) [45]. NMMO is prepared by the acetyl nitrate nitration of 3-hydroxymethyl-3-methyloxetane (HMMO) (Scheme 6). The synthesis of BAMO involves treating 3,3-bis(chloromethyl)oxetane (BCMO) with sodium azide in dimethylformamide at 85 °C for 24h (Scheme 7) [46]. AMMO, the monofunctional analog of BAMO, is synthesised by azidation with sodium azide of the chloro or tosylate [47] product of 3-hydroxymethyl-3-methyloxetane, HMMO (Scheme 8).



Scheme 6. Synthesis of NMMO



Scheme 7: Synthesis of BAMO

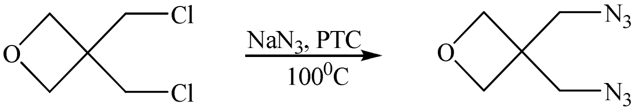


Scheme 8: Synthesis of AMMO

A more convenient synthesis of NMMO can also be carried out using an alternative nitrating agent, dinitrogen pentoxide (N_2O_5) [48] in a flow nitration system. This nitration process gives excellent yields and produces sufficiently pure NMMO that requires no further purification [49]. NMMO is a low Tg monomer ideal in many munitions applications, BAMO is a solid symmetric monomer (m.p. ~80^0C) ideal for use as the hard block in TPE manufacture,while AMMO is an unsymmetrical monomer used to provide amorphous character. The energetic monomers described above are readily polymerized to liquid curable prepolymers by use of a boron trifluoride etherate/1,4-butanediol initiator.

3.2.1 Poly BAMO

Polymerization of substituted oxetanes can produce polymers with higher molecular weight and higher elongation as compared to GAP. The functionality and molecular weight of the resulting polymer may be controlled easily as compared to epoxides [50]. Therefore, polymers and copolymers of oxetanes containing azido groups, such as AMMO and BAMO have been investigated in the past. The synthesis of polyBAMO has been carried out using two different procedures (Scheme 9) [51].



Scheme 9: Synthesis of BAMO

3.2.1.1 PolyBAMO properties

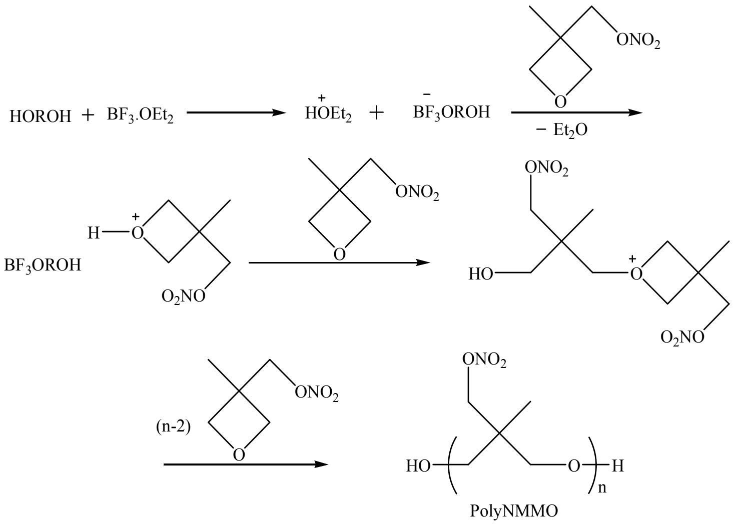
Oxetane based polymers such as polyBAMO [52] offer low glass transition temperature. The homopolymer of BAMO, though an energetic polymer is a solid which cannot be used directly for binder applications. But the copolymers of BAMO show good mechanical properties [53,54].

Table 3: Typical properties of polyBAMO

PolyBAMO	
Tg, ^{0}C	-45
Heat of formation, Kcal/mol	470
Functionality	2
Hydroxy value(mg KOH/g)	81

3.2.2 PolyNMMO

Traditionally, the polymerization of oxetanes to polyethers is achieved by cationic polymerization employing initiators (commonly diols) and catalyst (Lewis acid) [55]. The mechanism of polymerizing NMMO with boron trifluoride etherate catalyst is shown in scheme 10 and gives pale yellow liquid elastomers.



Scheme 10: Mechanism of polymerization of NMMO

Polymerization occurs by donation of proton from initiator to the oxetane, which undergoes propagation with more oxetane monomers to generate the polymer chain [56-60]. The polymer is terminated either with water or alcohol to give the hydroxyl terminated polymer.

3.2.2.1 PolyNMMO Properties

Oxetane based polymers, such as polyNMMO, offer low glass transition temperatures and miscibility with similar plasticzers, and are cured with conventional isocyanates upon heating. PolyNMMO has an intrinsic energy content of 818 kJ/kg and is classified as a non-explosive [61]. Table 4 highlights relevant properties of commercial polyNMMO, both difunctional and trifunctional species.

Table 4: Properties of Difunctional and Trifunctional PolyNMMO

Properties	Difunctional	Trifunctional
Mw	17000	6500
Mn	12500	4200
Mw/Mn	1.36	1.55
Functionality	≤2	≤3
Tg(DSC)	-30^{0}C	-35^{0}C
Onset decomposition	187^{0}C	184^{0}C

Aging and degradation studies on polyNMMO showed that polyNMMO exhibited gassing, although this can be reduced by the inclusion of stabilizers such as diphenylamine and 2-nitrophenylamine (1% wt/wt) [62]. Kinetic data obtained on polyNMMO decomposition followed first order rate laws with no autocatalysis observed. The activation energy is in the range associated with the decomposition by nitrate ester bond cleavage [63].

3.3 Fluorinated Polymers

Fluorinated polymers offer intrinsic advantages over inert hydrocarbons such as HTPB. Fluorocarbons have higher densities which result in formulations with higher densities and inherently higher performance [64]. Secondly, replacement of hydrogen (a fuel) on the polymer backbone with fluorine (an oxidant) increases the overall oxygen balance of the composition, again enhancing performance. One of the main types of fluorinated polymers are the polyformals. Polyformals are synthesised by the reaction of dihydric alcohols with formaldehdye to yield hydroxyl terminated polymers. A general reaction scheme for the production of polyformals is shown below [65].

$$\mathrm{HOCH_2(CF_2)_nCH_2OH} \xrightarrow[\mathrm{H^+}]{\mathrm{CH_2O}} \mathrm{HOCH_2[(CF_2)_nCH_2OCH_2O]_nH} + \mathrm{H_2O}$$

Polymers with various chain lengths have been prepared having low Tg and find use as copolymers with other low Tg monomers. In a US Patent, Adolph [66]has described an energetic binder comprising of

$$\mathrm{HO}—\mathrm{CH_2(CF_2)_nCH_2[OCH_2OCH_2(CF_2)_nCH_2]_m}—\mathrm{OH}$$

which is a hydroxyl terminated polyfluoroformal prepolymer with molecular weight between 1,000 and 10,000, and a compatible energetic plasticizer such as bis (2-fluoro- 2,2-dinitroethyl)formal. The increased compatibility of the prepolymer with fluorinated plasticizer is due to the presence of the formal moieties in the polymer backbone. The composition is cast-cured with polyisocyanates to give rubber-like polymers [67]. The novelty of this patent lies in the use of fluorinated polymers/plasticizers to form HMX-containing PBXs of the same energy (detonation pressure) as conventional nitrated polymers/plasticizers with HMX. The fluorinated polymers are believed to possess greater chemical and thermal stability than the polynitro polymers, although information in the open literature is scarce.

In addition to fluorine itself, several functional groups have been considered as explosophores, including the fluorodinitroethyl and difluoramine groups. Molecules with a single difluoroamine group tend to be sensitive and unstable, and this has been attributed to lability of the α-hydrogens; geminal bis(difluoramines) are typically less sensitive and more stable [68]. The difluoroamine group is also a potent oxidizing functional group, although the univalent fluorine is half as effective as divalent oxygen in providing a stoichiometric combustion balance [69]. Furthermore, diflouroamine groups are relatively sensitive to impact.

4. Energetic Plasticzers

The primary role of energetic plasticizers in energetic material formulations is to modify the mechanical properties of the mixture to improve safety characteristics. This is achieved by softening the polymer matrix and making it more flexible. In addition to improving properties such as tensile strength, elongation, toughness and softening point (Tg point), the plasticizer can have secondary roles [70]. These roles include a reduction of mix viscosity to ease processing, modification of oxygen balance and energy content, and in the case of propellants, burn rate modification to tailor ballistics.

To fulfill these roles, plasticizers require certain characteristics, such as:

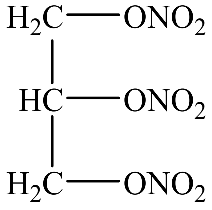
- a positive influence on safety and performance
- a positive influence on mechanical properties
- chemical and physical compatibility with all ingredients
- chemical stability and absence of toxicity

- absence of volatility and exudation (migration)
- low environmental impact
- availability and affordability.

By their own nature, plasticizers are typically oligomeric materials that have number average molecular weights ranging from 200 to 2000 [71]. Plasticizers with molecular weights above 2000 tend to be viscous, with properties more akin to the polymer matrix. Those with molecular weights below 200 may be more effective in reducing Tg, but they are highly volatile and tend to migrate out of a formulation readily (exudation). Number average molecular weights of plasticizers between 400 to 1000 are considered to give optimum plasticizing effect. Like their polymeric counterparts, plasticizers can be inert (non-energetic) or energetic. Non-energetic plasticizers are effective in improving mechanical properties, but degrade the output of the formulation by reduction of the overall oxygen balance [72]. Examples of non-energetic plasticzers include the esters, acetyl triethyl citrate, diethyl adipate, diethyl sebacate and dioctyl adipate. Similar improvements in mechanical properties are desired from energetic plasticzers, but with a contribution to the oxygen balance and/or energy of the formulation. Energetic plasticzers are typically nitro compounds or nitrate esters. Structural similarity with the energetic polymer should facilitate incorporation. However, one of the most common problems has been exudation, migration of the volatile low molecular weight plasticzer to (and from) the surface of the formulation. A promising recent approach has been to increase the structural similarity, and hence miscibility, by using low molecular weight oligomers of the polymer matrix as the plasticizer [73].

4.1 Nitrate Ester Plasticzers

The first energetic plasticzer for commercial explosives, nitroglycerine (NG) or glycerol trinitrate [74], is a high performance nitrate ester having the following structure (Figure 9)



$$\begin{array}{r l} H_2C & -ONO_2 \\ | & \\ HC & -ONO_2 \\ | & \\ H_2C & -ONO_2 \end{array}$$

Figure 9: Nitroglycerine

First discovered in 1846, nitroglycerine is a sensitive explosive easily initiated by friction and impact. When heated above 200 ºC, it will explode, while upon storage it proves unstable at temperatures exceeding 70-80 ºC [75]. In addition, NG exhibits significant physiological effects, causing dilation of the arteries and severe headache. Nevertheless, nitroglycerine still remains an effective plasticzer for many applications. The nitrate esters have proved to be a fertile source of energetic plasticizers. Some of the major nitrate esters in use today include trimethylol ethane trinitrate (MTN or TMETN), triethyleneglycol dinitrate (TEGDN), ethyleneglycol dinitrate (EGDN or nitroglycol), and butanetriol trinitrate (BTTN) (Figure 10). Being structurally similar to NG, they were developed to replace this material; most of these molecules possess some of NG properties without the severe hazards of NG.

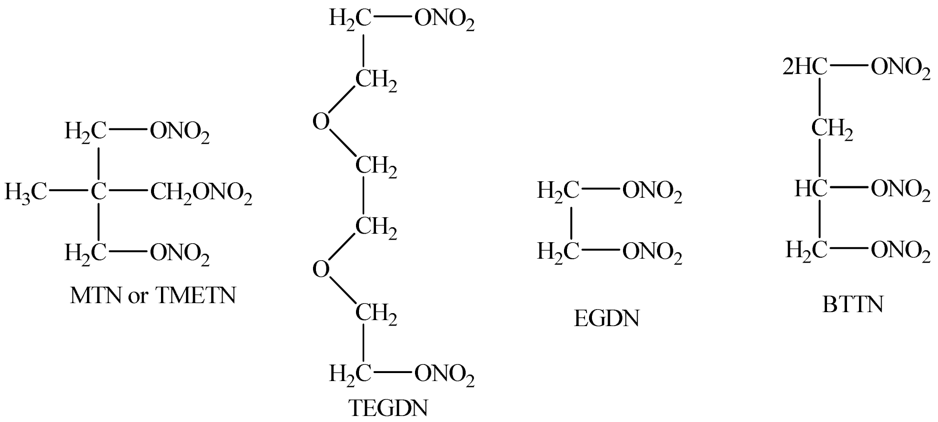


Figure 10: Structure of MTN, TEGDN, EGDN and BTTN

MTN or TMETN is chemically stable, insoluble in water and has low volatility. TEGDN is also chemically stable and has less impact sensitivity than NG and is less volatile than EGDN. EGDN is a more efficient plasticizer of NC than NG, has more energy but is also sensitive to impact. It possesses a lower density and a greater volatility than NG. BTTN is often used in propellants as a replacement for NG [76]. It has a lower density than NG but offers improved stability. Most of the energetic nitrate esters are explosives that possess low critical diameters, high volatility and high sensitivity, making them difficult to handle.

4.2 Azido Plasticzers

The poor mechanical properties of azide functional polymers like GAP can be improved markedly by incorporation of energetic azido functional plasticizers [77]. The synthesis of low molecular weight azido polymers such as GAP plasticizers can be achieved in a single process involving azide displacement of chlorine from epichlorohydrin monomer, ECH, followed by polymerization without the need for a catalyst [78]. GAP plasticizers are compatible with GAP polymer, as are nitrate esters such as butanetriol trinitrate, BTTN and trimethylol ethane trinitrate, TMETN. Properties of GAP diol and triol plasticizers are given in Table 5.

Table 5: Properties of GAP Plasticizers

Properties	GAP Diol	GAP Triol
ΔH_f, cal/g	+280	
Density, g/cm^3	1.29	1.29
Color	Light yellow	Light yellow
Mn	1700± 300	≥900
Functionality	2.0	2.5- 3.0
Thermal Stability	≥3	≥3
Tg, ^{0}C	-45	-45

As a general rule, plasticizing effect will be lost if terminal hydroxyl groups on the plasticizer react with the isocyanate crosslinking agent, effectively tying the plasticizer into the crosslinked polymer matrix. With this in mind, Ampleman [79] developed the synthesis of an azide terminated glycidyl azide plasticzer (GAPA), a plasticzer having no reactive terminal hydroxyl groups available for isocyanate cure. GAPA (Figure 11) is a pale yellow liquid with low molecular weight, low Tg and good stability. Properties of GAP diol and triol plasticzers are given in Table 6.

Table 6: Properties of Azido-Terminated GAP Plasticzer (GAPA)

Properties of Azido terminated GAPA	
ΔHf, cal/g	+550
Density, g/cm^3	1.27
Color	Light yellow
Mn	700-900
Thermal Stability	≤3
Tg, ^{0}C	-56

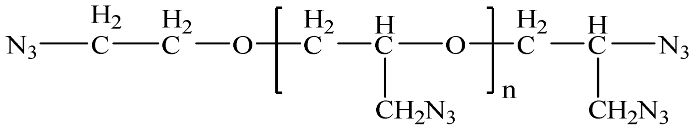


Figure 11: Structure of GAPA

4.3 K10 Plasticzer

K10, also known as Rowanite 8001, is a nitroaromatic plasticzer consisting of a mixture of 2, 4-dinitroethylbenzene and 2,4,6-trinitroethylbenzene (65%/35%). K10 (Figure 12) is manufactured by Royal Ordnance in the UK, and finds use as an energetic plasticzer in polymer bonded explosives. K10 is a clear, yellow/orange liquid with UK hazards classification of 6.1 (toxic). Compatibility issues with K10 include sensitivity to lead azide and other primary explosives [80].

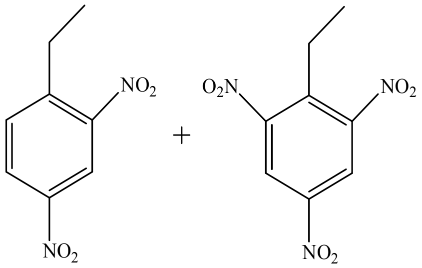


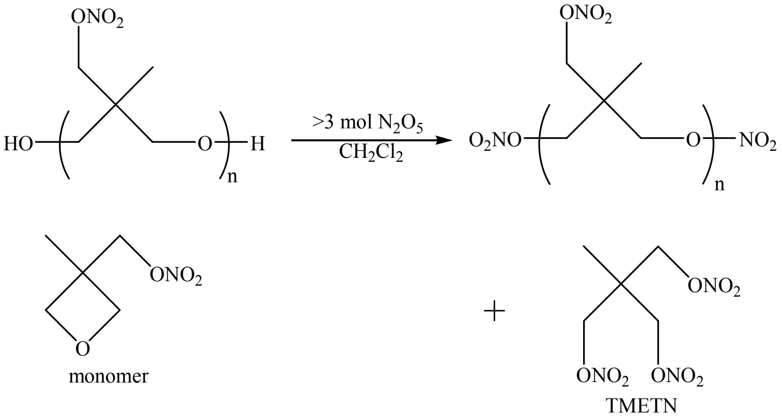
Figure 12: Structure of K10 plasticizer

4.4 Oxetane Plasticzers

Migration of the plasticzer is one of the major problems encountered with the use of energetic binder systems for explosive and propellant formulations. A recent approach has been to design plasticzers that resemble even more closely the polymer matrix, enhancing physical and chemical compatibility and, hopefully, minimising migration [81]. Melting point and glass transition temperature are clearly the most critical criteria, but other important considerations include energy balance, energy content and safety. A cyclic tetramer of NMMO which is also present in commercial polyNMMO (5-

10%), has a relatively high Tg and is not an effective plasticzer. Linear NMMO oligomers (polymers consisting of between 1-10 monomer units) were therefore prepared for use as plasticzers in polyNMMO binder systems. Oligomeric NMMO has a lower Tg than the cyclic tetramer but still contains NMMO monomer [82].

In order to remove the terminal hydroxyl groups, and prevent unwanted reaction with the isocyanate crosslinking agent, oligomeric NMMO has been further nitrated (nitration also increases the oxygen balance and enhances the energy of the binder system). Nitration with N_2O_5 for 30 minutes at 10°C gave clean conversion to nitrato terminated oligomers without sign of chain scission. Nitration with excess N_2O_5 also converts residual NMMO monomer into TMETN (scheme 11) [83].

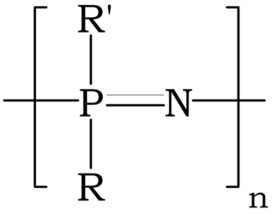


Scheme 11: Synthesis of TMETN

5. Polyphosphazenes

Current, in-service, energetic binders are typically linear carbon-based polymers which display low energy densities and relatively high glass transition temperatures (Tg) [84]. The high Tg of the binder usually requires the addition of a suitable plasticizer to the final PBX compositions in order to lower the Tg to an acceptable level. Although plasticisation is a viable solution to reduce the binder's high Tg, it also leads, in time, to the migration of plasticizer to the surface of the explosive filler, with the effect of seriously compromising the low-temperature performance of the PBX. One of the main problems with energetic binders is therefore the difficulty in developing materials which display high energy-densities and low Tg, a combination of properties which would ultimately allow the formulation of PBXs of higher solid loading and yet good physical and IM properties. In search of a viable alternative to carbon-based binders [85], novel systems based on a *linear polyphosphazene* backbone are currently under investigation as potential high-density, high-energy density (HED) and low Tg binders for new, polymer bonded explosive compositions.

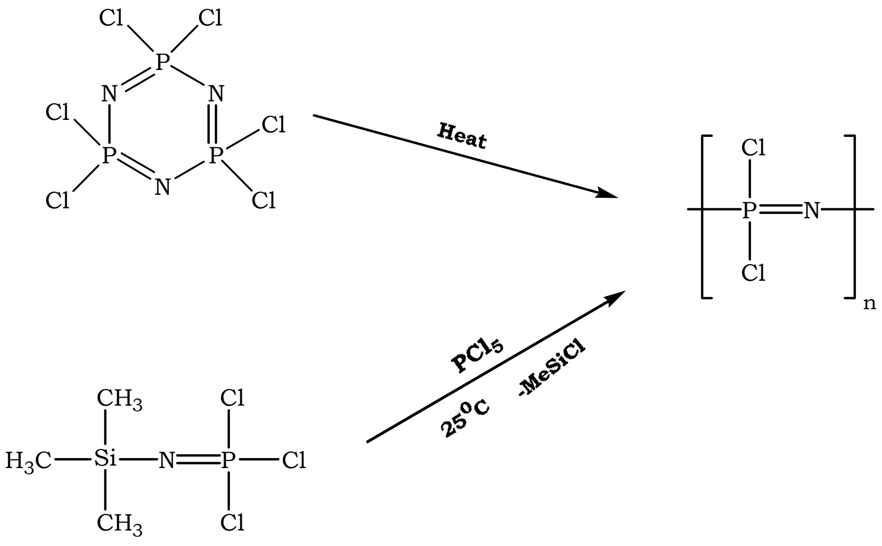
Polyphosphazenes are a unique class of polymers developed primarily by H. Allcock at Penn State during the 1960's [86]. Polyphosphazenes represent the single largest class of polymers and are differentiated from most conventional polymers by their route of synthesis, their synthetic versatility, tunable hydrolytic degradability, high thermal and oxidative stability and broad range of physical, chemical and mechanical characteristics. Due to their unique synthetic pathway, polyphosphazenes offer the promise of circumventing many of the issues associated with classical polymerization [87]. Polyphosphazenes are having low glass transition temperatures, and thus providing good low temperature properties, because of the flexibility of the polyphosphazene backbone. Energetic Polyphosphazenes [88] are of potential interest as novel binders for energetic formulations. Polyphosphazenes consist of an inorganic phosphorous-nitrogen [89] backbone and reactive pendant side groups that may be organic, organometallic or inorganic in nature [90]. In energetic polyphosphazenes, highly energetic side groups of the backbone are substituted with chosen building blocks through well-established methods of organic chemistry.



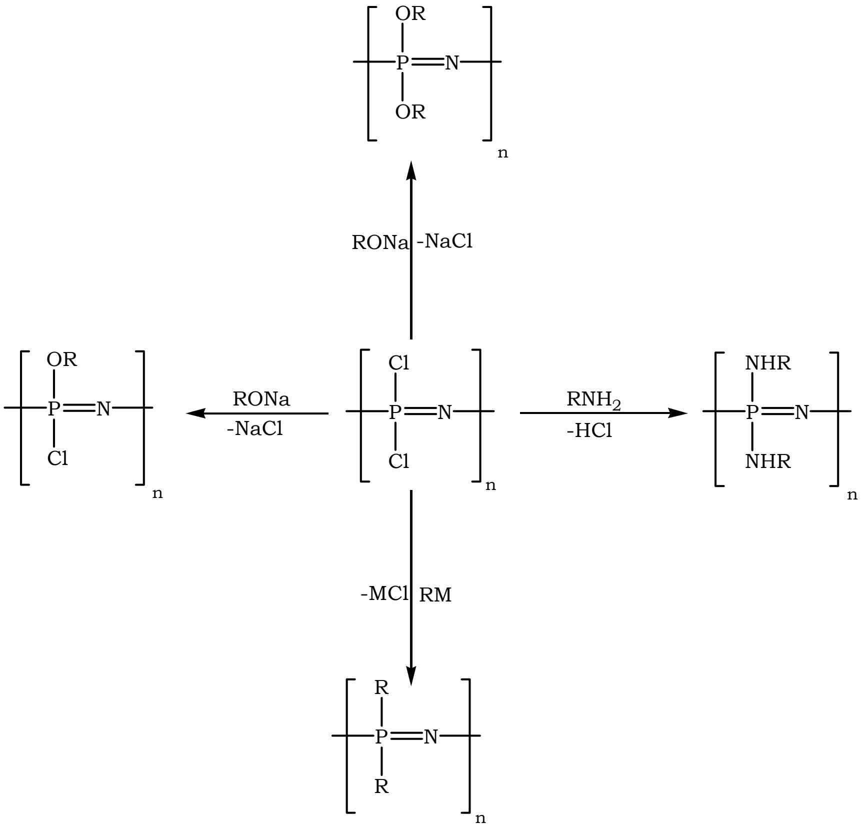
R,R' = OC_6H_5, OCH_2F_3, OCH_2CF_3 etc.

Figure 13: General structure of Polyphosphazene.

Energetic binders based on polypohsphazenes have low glass transition temperatures without the need for plasticization, to avoid rigidity at low temperature. The current binder system uses the energetic polyGLYN, polyNMMO, polyBAMO and copolymers of BAMO, GLYN, and NMMO etc. The high reactivity of the PCl_2 groups in polyphosphazenes has enabled them to convert the polymer by wide variety of nucleophiles to a large number of organo-substituted polyphosphazenes [91].



Scheme 12: Synthesis of polyphosphazene



Scheme 13: Reaction scheme for the synthesis of poly(diorganophosphazenes)

As in the above scheme, substitution reactions on $(NPCl_2)_n$ are in general carried out with alcohols and amines. Halogen replacement in $(NPCl_2)_n$ and $(NPF_2)n$ by treatment with organometallic reagents is accompanied with competing side reactions as skeletal cleavage and crosslinking [92,93]. The synthesis poly(diorganophosphazenes) with all substituents linked to the polymer backbone by a direct P-C bond is therefore not possible via this route. In another approach, $(NPCl_2)_3$ is allowed to react first with the organometallic reagents and the partly organo-substituted cyclic trimer can be converted to a high polymer in a similar manner as $(NPCl_2)_3$. Fully organo-substituted cyclophosphazene like $(NPMe_2)_3$ or $(NPPh_2)_3$ undergo ring –ring equilibration reactions but polymers are not obtained [94].

The thermal ring-opening polymerization of the mixed rings takes place at much lower temperature range from 90 to 180^0C whereas for $(NPCl_2)_3$,a temperature of 250^0C is needed [95]. The chlorine atoms in these polymers can also be replaced by various nucleophiles, which mean that these polymers stand the basis of a new class of polymers.

5.1 High Performance Elastomers

Polyphosphazenes have several attributes that make them valuable for aerospace, energy, or oil drilling applications. These properties include low temperature flexibility and elasticity; resistance to hydrocarbon fuels, oils, and hydraulic fluids; fire resistance, radiation resistance, and ultraviolet stability. The specific applications fall into four main categories based on (1) elastomeric properties, and (2) fire-resistant composite materials and foams [96,97].

5.1.1 Phosphazene Elastomers

This is one of the most established uses for polyphosphazenes. Although polyphosphazenes are known with glass transition temperatures that range from -100°C to more than +200°C, species with fluoroalkoxy and/or organosilicon side groups with glass transitions in the -60°C range are of special value in aerospace, automotive, arctic, and oil drilling engineering. They are used to fabricate O-rings, seals, and shock-absorbing devices for low temperature uses. The presence of two or more different types of side groups in these polymers ensures a lack of crystallinity and provides the molecular free volume needed for elasticity [98]. The fluoroalkoxy derivatives are also noted for their ability to absorb and dampen impact energy, a valuable property for certain applications.

6. Materials and Methods

6.1 Analytical Equipment and Methods

6.1.1 UV-Vis spectra

UV spectra of the polymers PECH and GAP were recorded using Thermo Evolution 201 UV Visible spectrophotometer. Samples were dissolved in dichloromethane, in concentrations of 1 mg/ml.

6.1.2 FTIR spectra

FTIR spectra of polymers were recorded with a JASCO FT-IR 4000 instrument. The FTIR spectra were recorded in the range from 500 to 4000 cm^{-1} using 32 scans. FT-IR spectra were recorded by the KBr pellet method and liquid samples were on the NaCl crystal.

The presence of nitro, azido, hydroxyl groups and ether linkages etc. are identified from FT-IR spectra [99].

6.1.3 NMR analysis

NMR spectra were recorded on a Bruker Avance III, 400MHz spectrometer operating at 400 MHz for ^{1}H spectra, 162 MHz for ^{31}P spectra and 100 MHz for ^{13}C spectra. Standard pulse sequences were used for obtaining ^{1}H, ^{31}P and ^{13}C spectra. NMR spectroscopy remains one of the most effective analytical tools available to binder chemists as it accurately elucidates structure and purity for both monomer and polymer. Various NMR nuclei can be readily examined, with proton and carbon NMR (^{1}H and ^{13}C) the most frequently used techniques [100]. Samples were dissolved in $CDCl_3$ and dueterated acetone. ^{1}H NMR was recorded with reference to TMS and ^{31}P NMR was recorded with 85% H_3PO_4 as external standard.

6.1.4 GPC analysis

The average molecular weight and molecular weight distribution have great influence on physical properties of the energetic binders. These parameters are readily measured by gel permeation chromatography, GPC, vapour phase osmometry or light scattering techniques. Typically, GPC is used mainly for determining molecular weight, although light scattering techniques, in particular low angle laser light scattering are becoming more popular.

The separation of components of a polymer by GPC is a result of size exclusion of the polymer molecule or a difference in molecular size in solution, where the larger molecules are found in the early elution volume [101]. The molecular size (or hydrodynamic radius) of a polymer component depends upon molecular weight, chemical composition, molecular structure and experimental parameters (solvent, temperature and pressure) and requires accurate calibration by GPC polymer standards.

Molecular weights were found out by WATERS GPC consisted of a Waters 717 Plus auto sampler, a Waters 600E system controller (run by Empower software), and a Waters 610 fluid unit. Waters 410 differential refractometer was used as the detector at 35 ^{o}C. Toluene (HPLC grade) was used as eluent at a flow rate of 1 ml/min and typically 5 mg of sample was dissolved in 1 mL of solvent for analysis. The column oven was kept at 30^{0}C and the injection volume was 100 µm. Two PLgel 5 µm Mixed-C columns and a pre-column (PLgel 5 µm Guard) were used. A set of narrow molecular weight polystyrene samples covering a molecular weight range of 350 - 3,50,000 were used as GPC standards. All molecular masses are reported as polystyrene equivalents [102].

6.1.5 DSC analysis

Differential Scanning Calorimetry (DSC) measures the temperature and heat flow associated with transitions in materials as a function of time and temperature in a controlled atmosphere. These measurements provide quantitative and qualitative information about physical and chemical changes that involve endothermic or exothermic processes, or changes in heat capacity [103].

DSC analyses of polymer samples were performed with TA Instruments DSC-Q100. Indium metal was used for the calibration of the instrument according to standard procedures. The analysis was carried out under nitrogen atmosphere and 10^0 C/min was used as heating rate. About 1-3 mg of sample was taken in aluminium sample pan for analysis.

6.1.6 Density of the Polymer

The mass of an irregular solid is determined by weighing. When the solid is placed in a pykcnometer filled with a liquid of known density [104], the volume of the liquid which will overflow is equal to the volume of the solid. The mass of the liquid which will overflow is determined as the difference between the sum of the mass of the pykcnometer filled with liquid plus the mass of the solid and the mass of the pykcnometer filled with liquid after the solid has been placed inside. The volume occupied by this mass is determined from the known density of the liquid. It is necessary that the solid be insoluble in the liquid used. The density of the solid is determined from these measurements of mass and volume.

Density is defined as the ratio of the mass of a body to its volume. Its experimental determination requires the measurement of these two quantities for the selected piece of material.

6.1.7 Hydroxyl Value of the Polymer

The hydroxyl value of the polymer was estimated by treating 2 ml of standard acetylating agent (66 ml pyridine/ 33 ml acetic anhydride) for 15 min at 95^{0}C. Each analysis was compared with a blank by titrating with 0.1 N potassium hydroxide. The difference in titrant between sample and blank was used to calculate the hydroxyl value of the polymer [105].

Let, weight of polymer used = Z g
Flask A (Blank) requires = X ml of KOH
Flask B requires = Y ml of KOH
B-A = ml of KOH
B-A ml of KOH = B-A/1000 Hydroxyl group
Hydroxyl value of the polymer = B-A/1000 x Mol.Wt. of Polymer/ Wt. of polymer taken

6.1.8 Heat of formation

The derivation of the standard enthalpy of formation of an organic compound requires the experimental measurement of its standard enthalpy of combustion, [106] ΔH^oc. If the combustion reaction under calorimetric investigation is carried out under constant-volume conditions, as in a pressurised steel vessel (bomb) [99-102] no work of expansion can be performed and the heat of the reaction will be equal to the internal energy change ΔUc. Only if a constant pressure apparatus is used, the measured heat of reaction would, by definition, be equal to the enthalpy change of reaction. From combining the First Law of Thermodynamics with the ideal Gas Law, an equation can be derived which effectively describes the difference between ΔUc and ΔHc for a given reaction.

$$\Delta Hc = \Delta Uc + \Delta(PV)$$

Assuming the Ideal Gas Law to apply at the typical oxygen bomb pressure (30atm), then Δ(PV) will be equal to ΔnRT and the above equation can thus be written as

$$\Delta Hc = \Delta Uc + \Delta nRT$$

Where Δn is the difference between the gaseous moles of products and reactants, R is the universal gas constant and T is the absolute temperature. If all reactants and products are solids or liquids, the change in volume which accompanies a reaction at constant pressure is very small, usually less than 0.1%,and the magnitude of the thermal contribution due to expansion work of condensed matter is usually less than 5 J [107]. This error can be included in the overall experimental uncertainty interval, which, for most experimental determinations, is usually far greater. For reactions at very high pressures, however (e.g. at the bottom of the ocean or deep in the Earth's fluid mantle), Δ(PV) can be significant even for condensed phases. When gases are involved in the reaction, however, an appreciable value of Δ(PV)can occur and the difference between internal energy and enthalpy of reaction canbe significant [108].

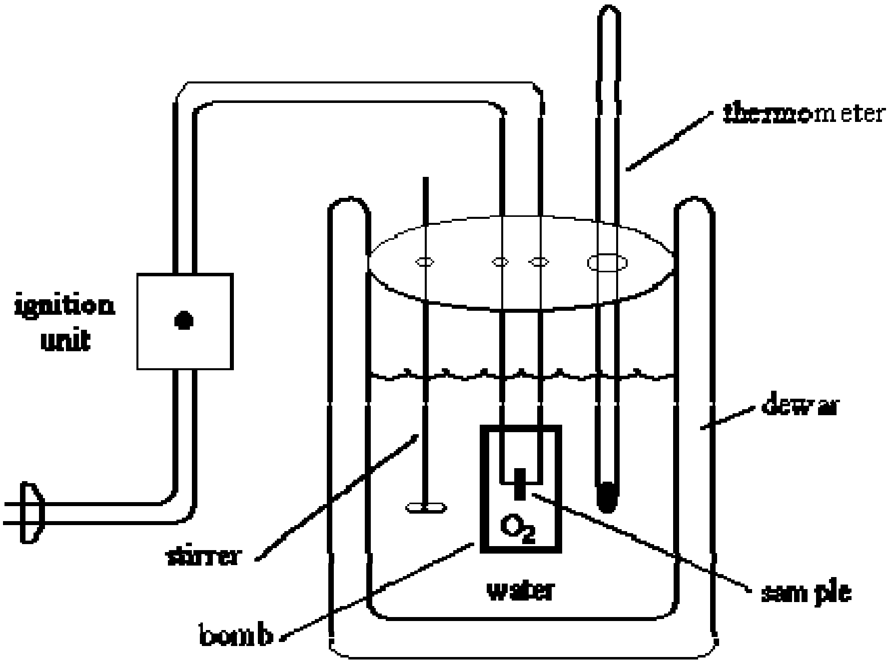
6.1.9 Bomb Calorimeter

Bomb calorimetry is used to determine the enthalpy of combustion, $\Delta_{comb}H$, for hydrocarbons: [109]

$$C_xH_YO_{Z\,(s)} + (2X+Y/2-Z)/2\ O_{2\,(g)} \rightarrow X\ CO_{2\,(g)} + Y\ H_2O_{(l)}$$

Since combustion reactions are usually exothermic (give off heat), $\Delta_{comb}H$ is typically negative. (However, be aware that older literature defines the "heat of combustion" as - $\Delta_{\text{comb}}H$, so as to avoid compiling tables of negative numbers!)

6.1.9.1 Construction of a Bomb Calorimeter



The bomb calorimeter consists primarily of the sample, oxygen, the stainless steel bomb, and water.

The dewar prevents heat flow from the calorimeter to the rest of the universe, *i.e.*,

$$q_{\text{calorimeter}} = 0$$

Since the bomb is made from stainless steel, the combustion reaction occurs at constant volume and there is no work, *i.e.*,

$$w_{\text{calorimeter}} = -\int p \, dV = 0$$

Thus, the change in internal energy, ΔU, for the calorimeter is zero

$$\Delta U_{\text{calorimeter}} = q_{\text{calorimeter}} + w_{\text{calorimeter}} = 0$$

The thermodynamic interpretation of this equation is that the calorimeter is isolated from the rest of the universe.

6.1.9.2 ΔU and ΔH in a Bomb Calorimeter

6.1.9.2.1 Internal energy change ΔU

Since the calorimeter is isolated from the rest of the universe, we can define the reactants (sample and oxygen) to be the system and the rest of the calorimeter (bomb and water) to be the surroundings. [110]

The change in internal energy of the reactants upon combustion can be calculated from

$$dU_{tot} = dU_{sys} + dU_{surr} = 0$$

$$dU_{sys} = - dU_{surr}$$

$$= -[(\partial U/\partial T)_V\, dT + (\partial U/\partial V)_T\, dV]$$

Since the process is at constant volume, $dV=0$. Thus, recognizing the definition of heat capacity C_v yields

$$dU_{sys} = - C_V dT$$

Assuming C_v to be independent of T over small temperature ranges, this expression can be integrated to give

$$\boxed{\Delta U = -C_V \Delta T}$$

where C_v is the heat capacity of the surroundings, *i.e.*, the water and the bomb.

6.1.9.2.2 Enthalphy change ΔH

By definition of enthalpy

$$\Delta H = \Delta U + \Delta(pV)$$

Since there is very little expansion work done by condensed phases, $\Delta (pV) \approx 0$ for solids and liquids. Assuming the gas to be ideal, yields

$$\boxed{\Delta H = \Delta U + RT\Delta n_{gas}}$$

6.1.9.2.3 Intuitive difference between ΔU and ΔH

If $\Delta U = q_v$ is the heat flow under constant volume conditions, and $\Delta H = q_p$ is the heat flow under constant pressure conditions. The difference between these two situations is that pV work can be done under constant pressure conditions, whereas no pV work is done under constant volume conditions [111].

Consider the case where $\Delta n_{gas} > 0$. *i.e.*, the system expands during the reaction. The same amount of energy is released by the reaction under both sets of conditions. However, some of the energy is released in the form of work at constant pressure; thus, the heat released will be less than at constant volume. Mathematically,

heat released < energy released

$$-\Delta H < \Delta U$$

$$\Delta H > \Delta U$$

In the case where $\Delta n_{gas} < 0$. *i.e.*, the system contracts during the reaction, the surroundings does work on the system. Thus, this work is available for energy release from the system back to the surroundings in the form of heat. Mathematically,

heat released >energy released

$$-\Delta H > \Delta U$$

$$\Delta H < \Delta U$$

6.1.9.3 Calibration of the Calorimeter

6.1.9.3.1 Estimating C_v

The heat capacity of the bomb calorimeter can be estimated by considering the calorimeter to be composed of 450 g water and 750 g stainless steel [112]. Knowing the specific heat capacity of water to be 1 cal/g·K and estimating the specific heat capacity of steel to be 0.1 cal/g·K yields,

$$C_V(\text{Calorimeter}) = m(\text{water}) \times C_V(\text{water}) + m(\text{steel}) \times C_V(\text{steel})$$

$$= 450\text{g}\ (1\text{Cal/gK}) + 750\text{g}\ (0.1\text{Cal/gK}) = 525\text{Cal/K}$$

6.1.9.3.2 Measuring C_v

For accurate work, the heat capacity of the calorimeter must be measured. This is done by depositing a compound having known amount of energy into the calorimeter and observing the temperature increase [113]. The two most common methods for measuring C_v are

1. Burning a standard with known ΔU, *e.g.*, benzoic acid.

$$m_{\text{benzoic acid}}\,\Delta U_{\text{benzoic acid}} = m_{\text{benzoic acid}}\ \text{-6318 cal/g·K} = -C_v\,\Delta T$$

2. Doing electrical work by passing current though a resistor.

$$\Delta U = w + q = V \cdot I \cdot t + 0 = C_v\,\Delta T$$

6.1.9.4 Corrections in Bomb Calorimetry

6.1.9.4.1 Combustion of fuse

Nickel and iron fuses can burn according to

$$\text{Ni} + 0.5\ \text{O}_2 \rightarrow \text{NiO}$$

or

$$2\text{Fe} + 1.5\text{O}_2 \rightarrow \text{Fe}_2\text{O}_3$$

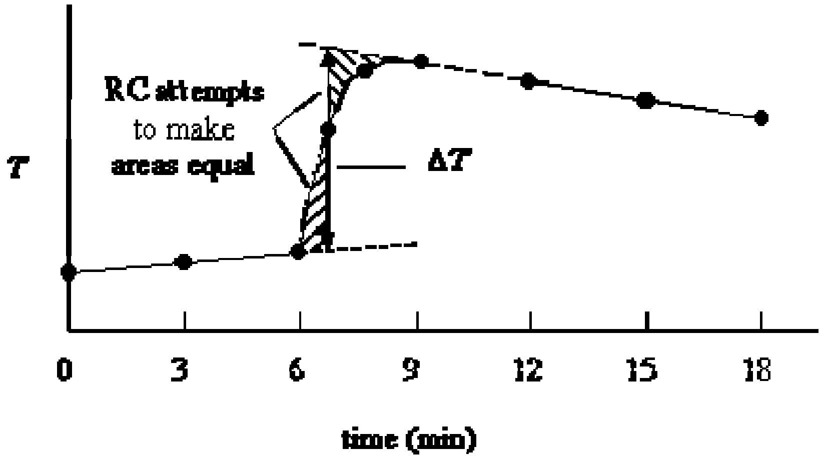
The heat released by combustion of the fuse is accounted for by recognizing that

$$\Delta U = \Delta U_{\text{sample}} \cdot m_{\text{sample}} + \Delta U_{\text{burned fuse}} \cdot m_{\text{burned fuse}} = -C_{\text{v}}\ \Delta T$$

where the mass of the burned fuse is determined by weighing the fuse before and after firing the bomb.

6.1.9.5 Nonadiabaticity of calorimeter

A bomb calorimeter is only approximately adiabatic. In reality, there is a small heat leak through the dewar ($q_{\text{calorimeter}}\ {}^{1}\ 0$) and the stirrer does work on the calorimeter ($w_{\text{calorimeter}}\ {}^{1}\ 0$). Nonadiabaticity is corrected for with an empirical radiative correction, *RC*.



The time at which the bomb is considered to be fired is the time that makes the areas indicated in the above figure equal. For the Parr calorimeter, this is estimated to be at $t = 7$ minutes. Thus, the temperature at $t = 6$ minutes must be extrapolated forward 1 minute by the pre-firing slope, and the temperature at $t = 12$ minutes must be extrapolated backward 5 minutes by the post-firing slope. Mathematically, this is done as follows

$$\Delta T = [T_{12} + (-5\ min)\ (T_{18}-T_{12})/6\ min] - [T_5 + (1\ min)\ (T_6-T_0)/6\ min]$$

$$= T_{12} - T_6 + [(-5\ min)\ (T_{18}-T_{12})/6\ min] - [\ (1\ min)\ (T_6-T_0)/6\ min]$$

$$= T_{12} - T_6 - [5(T_{18}-T_{12}) + (T_6-T_0)/6]$$

$$= T_{12} - T_6 - RC$$

6.1.9.6 Nitric acid formation

At high temperatures, nitrogen can form nitric acid in the presence of oxygen and water. (This reaction also occurs in automobile engines and is partially responsible for smog production.)

$$N_2 + 2.5O_2 + H_2O \rightarrow 2HNO_3$$

Flushing the bomb with oxygen prior to firing, thereby displacing all nitrogen, eliminates nitric acid formation.

6.1.9.7 Application of $\Delta_{comb}H$

In addition to measuring the energy release of one particular reaction, calorimetry is an important tool for determining the enthalpy of formation for the compound under study. This information can then be applied to any reaction involving the compound.

The enthalpy of combustion for the reaction can be written as

$$\Delta_{comb}H(C_xH_yO_z) = \nu(C_xH_yO_z)\Delta_fH°(C_xH_yO_z) + \nu(O_2)\Delta_fH°(O_2) + \nu(CO_2)\ \Delta_fH°(CO_2) + \nu(H_2O)\ \Delta_fH°(H_2O)$$

$$\Delta_{comb}H(C_xH_yO_z) = \nu(C_xH_yO_z)\ \Delta_fH°(C_xH_yO_z) + \nu(O_2)\ \Delta_fH°(O_2) + \nu(CO_2)\ \Delta_fH°(CO_2) + \nu(H_2O)\ \Delta_fH°(H_2O)$$

where $v(i)$ is the stoichiometric coefficient of i. Since $\Delta_f H°(C_xH_yO_z)$ and $\Delta_f H°(H_2O)$ are known (and $\Delta_f H°(O_2)$ equals zero), measurement of $\Delta_{comb} H(C_xH_yO_z)$ allows calcualtion of $\Delta_f H°(C_xH_yO_z)$.

7.Main Objectives of the present work

- Synthesize Oxirane based energetic polymers by classical cationic polymerization technique and activated monomer polymerization technique.
- Synthesize and characterize copolymers of the oxirane and oxetane
- Synthesis of novel polyphosphazene based energetic binders
- Evaluate the binder properties of the synthesized polymers, especially heat of formation of the polymers.

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Chapter 2

SYNTHESIS AND CHARACTERIZATION OF OXIRANE BASED ENERGETIC POLYMERS

Abstract

In an effort to comply with insensitive munitions (IM) criteria, energetic binders comprising of polymers and plasticizers are being used in cast-cured polymer bonded explosives and cast composite rocket propellants. Poly(epichlorohydrin) was prepared by the activated monomer cationic ring opening polymerization (CROP) of epichlorohydrin (ECH) using borontrifluorideetherate (BF_3-etherate) as catalyst and 1,4 butanediol as initiator.Poly(epichlorohydrin)-THF copolymer was prepared by the classical cationic ring opening polymerization of epichlorohydrin (ECH) and tetrahydrofuran (THF) with borontrifluorideetherate (BF_3-etherate) as catalyst. Both the polymerization reactions were terminated by the addition of water. Energetic binders such as glycidylazide polymer (GAP), poly(dinitropropanoxy)oxirane (PDNPO) and poly(bistrifluoroethoxy)oxirane (PBTEO) are used to maintain the overall energy of explosive formulations or improve their performance. Glycidylazide polymer with terminal hydroxyl groups (GAP-diol) were synthesized by the reaction of PECH-THF copolymer with sodium azide in organic solvent. PDNPO was synthesized by the nucleophilicsubstitution of glycidol to the PECH-THF copolymer followed by nitration and PBTEO was synthesized by the substitution of sodium salt of trifluoroethanol to the PECH-THF copolymer with a phase transfer catalyst. The GAP-THF diol, PDNPO and PBTEO diol obtained were characterized using different analytical techniques. Conversion of the chloromethyl groups of PECH-diol to azide groups and formation of PDNPO and PBTEO were confirmed using FTIR and ^1H &^{13}C NMR spectroscopy. Thermal analysis using DSC showed a glass transition temperature around -45^{0}C and exothermic decomposition around 242 ^{o}C for GAP-THF diol, a glass transition *temperature around -37^{0}C and exothermic decomposition around 210 °C for PDNPO and PBTEO showed a glass transition temperature of -49^{0}C and exothermic decomposition around 340^{0}C. The terminal hydroxyl groups of the polymers were estimated by acetylating them using acetic anhydride and pyridine and analyzing the remaining acid by titration.*

Keywords: *Ring opening polymerization, Polyepichlorohydrin, Glycidyl Azide polymer, Oxirane polymer.*

2.1 Introduction

Polyurethane materials, vital due to their versatile properties, are found in many applications in everyday life [1]. They are most generally prepared from the reaction of polyols with isocyanates [2]. However, today, researchers focus more and more on environmentfriendly chemistry [3,4]. One modification deals with the development of an isocyanate-free route to polyurethanes that would prevent the use of isocyanates and therefore of highly toxic phosgene involved in their synthesis. A possible reason for this is the decrease of fossil feedstock and the possibility of the use of natural products [5] as renewable raw chemicals. Among them, vegetable oils constitute an important feedstock, already used for the synthesis of biodiesel and as a source of green chemicals [6-9]. Glycerol, a by-product of both the biodiesel production and the saponification of animal fat is obtained in large amounts and needs to be better valorized as raw material. Its transformation into glycerol carbonate, aldehydes, ketones, and carboxylic acids [10], as well as epichlorohydrin (ECH) [11] and allylglycidyl ether [12] (AGE), were reported.

Production of ECH from glycerol via dichlorination and dehydrochlorination has been recently industrialized [13, 14]. AGE can be synthesized by the reaction of ECH with allyl alcohol, the latter being obtained by heating glycerol in the presence of formic acid. ECH and AGE possess two functional groups, which make these monomers of interest for the preparation of reactive polymers even if the first one is toxic. Polyepichlorohydrin (PECH) can be readily modified by chemical substitution of the chlorine atoms to yield a broad series of functional side chain polymers [15,16] and more particularly to the synthesis of poly(glycidylazide) used as precursor for energetic polyurethanes in the field of propellants [17].

The microstructure of PECH obtained from CROP depends on the type of initiator employed. Literature has reported three microstructures obtained from utilizing different initiators [18-21]. First, cationic initiators such as Lewis acids or tertiary oxonium salts, often complexed with water, alcohol or ether, result in an atactic low molecular weight polymer (Mn<4000) with hydroxyl end groups when polymerization is quenched with water or alcohol [22]. Second, telechelic polymers of molecular weight up to 15 000 can be obtained where 1,4-butanediyl ditriflate is used as initiator [23]. The important industrial method is the Vandenberg process, based on the use of organometallic initiators, which yields polymers of high molecular weight (rubber) that are often fractionated into atactic and isotactic components [25].

Current reduced-vulnerability explosives use cured binder systems that possess adequate dimensional stability and required energy absorbing properties, but are ultimately difficult to recover or recycle either during manufacture or demilitarisation. One such binder, hydroxyl terminated polybutadiene, HTPB [26] has excellent physical properties, but it is an inert binder. The binder dilutes the overall energy output of the composition leading to a lowering of explosive performance characteristics. As such, recent advances in propellant research are aimed at developing high energy binders which give better performance than the commonly used binder Hydroxyl terminated Polybutadiene (HTPB) [27, 28] and which are compatible with eco-friendly oxidizers, ammonium nitrate (AN), hydraziniumnitroformate (HNF) or ammonium dinitramide (ADN) [29-32]. Polymeric azides that include GlycidylAzide Polymer (GAP) and its copolymers contain azide groups along the polymer chain as pendent groups, which make them highly energetic. These polymers [33-35] can therefore be used as energetic binders having minimum smoke, reduced pollution and sensitivity. In addition to being fuel rich, these propellants liberate large amounts of Hydrogen, Nitrogen, CO and gaseous hydrocarbons on burning and provide high burning rate.

Not surprisingly, this has brought a shift in direction from inert to energetic binders. Energetic binders contain energetic chemical groups known as *explosophores*, typically nitro (C–NO_2) [1], nitramine (N–NO_2) [36-41], difluoroamine (-NF_2), azido (-N_3), and nitrate ester groups (–ONO_2). Such energetic binders impart to PBXs an increase in energy output, lower vulnerability and potential environmental benefits such as recovery and possible reuse of munitions [42-44]. In addition, it is expected that these new energetic binders will lend themselves well to insensitive munitions, where a lowering of vulnerability with incorporation of an energetic binder occurs.

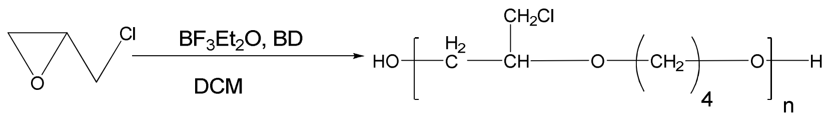
2.2 Results and Discussion

This section includes a description of the results obtained from the synthesis andcharacterization of PECH-diol, GlycidylAzide Polymer (GAP), poly(dinitropropanoxy)oxirane (PDNPO) and poly(bistrifluoroethoxy)oxirane (PBTEO).

2.2.1 Cationic ring-opening polymerization of epichlorohydrin

Polymerization of ECH by cationic ring-opening polymerization using a combination ofborontrifluorideetherate (catalyst) and low molecular weight diol (initiator) is reported toyield polymers with low cyclic oligomer formation. The use of a diol also affordsthe possibility of producing linear telechelics, when the polymerization is terminated withan alcohol or water. In this study, polymerization of ECH proceeded to a high conversion (90%) and yielded a polymer with a narrow polydispersityindex(1.1).

The ring-opening polymerization of epichlorohydrin monomer was carried out accordingto the published procedure described by Ivin [22]. Scheme 2.1is a representation of theprocedure followed for the cationic ring-opening polymerization of ECH monomer.



Scheme 2.1: Synthesis of PECH diol

A typical GPCprofile of a PECH-diol is shown in Figure 2.1. High yields and low molecular weightdistributions (MWD) could be an indication that polymerization proceeded in a reasonablycontrolled manner [13].

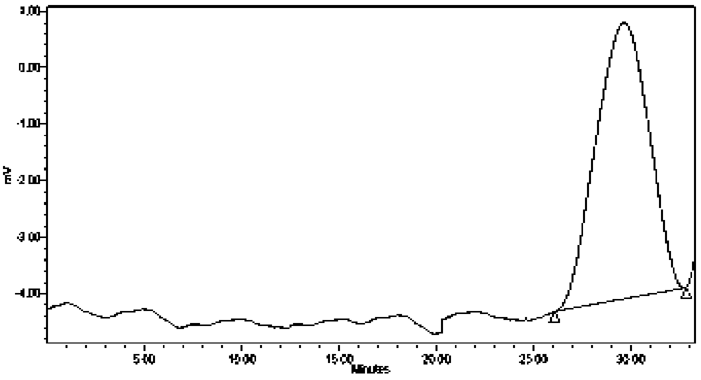


Figure 2.1:GPC trace of PECH-diol, Mn = 2224 and polydispersity index 1.1.

The UV-Vis spectrum of PECH-diol is shown in Figure 2.2. UV-Vis spectrum did not show anyabsorption peak for PECH-diol in the range of 600-200 nm, which indicates that thechloromethyl pendant groups do not have strong absorption at this UV-Vis range and it is transparent to UV-Vis region [9, 13].

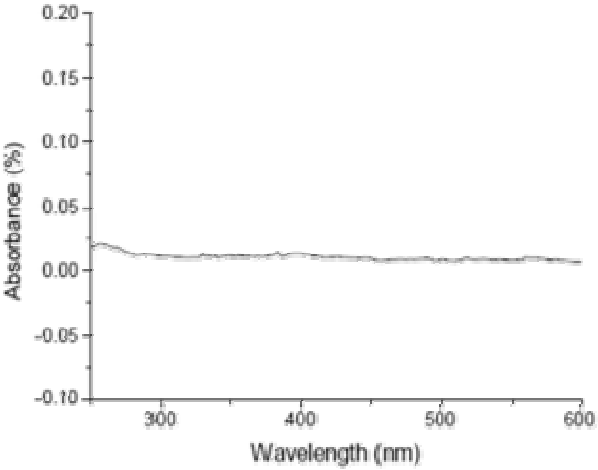


Figure 2.2:UV-Vis spectrum of PECH-diol

The FTIR spectrum is shown in Figure 2.3. The FTIR spectrum of PECH-diolcontains peaks indicative of important features of PECH-diol, namely absorption peaksat 745, and 1150 cm^{-1}, which correspond to chloromethyl group and polyether linkage,respectively. The absorption around 2850 and 3450 cm^{-1} could be attributed to methyland ethyl groups and the hydroxyl groups, respectively.

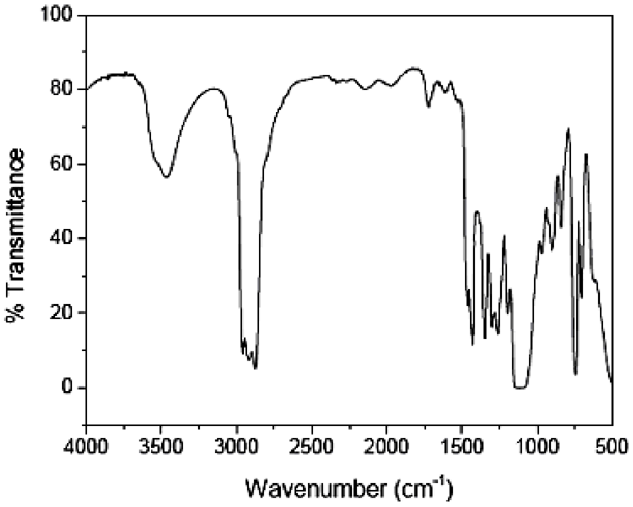


Figure 2.3:FTIR spectrum of PECH-diol

In an attempt to understand the microstructure of PECH-diol produced via CROP, NMRanalyses using^{1}H-NMR and ^{13}C-NMR were performed. The ^{1}H-NMR spectrum ofPECH-diol is shown in Figure 2.4, while Figure 2.5shows the ^{13}C-NMRspectrum.The important feature of ^{1}H-NMR spectrum is the signals around 1.6 and 3.1ppm, which correspond to the CH$_2$ protons of the 1, 4-butanediol included in the PECHdiol,and the hydroxyl group proton, respectively. The peaks between 3.6 and 4.0 ppmcorrespond to the PECH protons. The assignments of the PECH-diol structure areillustrated in Figure 2.5.Significant peaks of ^{13}C-NMR spectrum of PECH-diol are around 26-28 and at 75ppm. These peaks correspond to the CH$_2$ of the 1, 4-butanediol. Peaks around 43-46ppm is attributed to the chloromethyl group of PECH. The polyether linkage –O–CH$_2$–peaks appear around 69-71 ppm. On the other hand, solvent absorption appears at 77ppm and peak around79 ppm is attributed to the –O–CH–. The assignments of PECHdiolstructure are indicated in Figure 2.5.

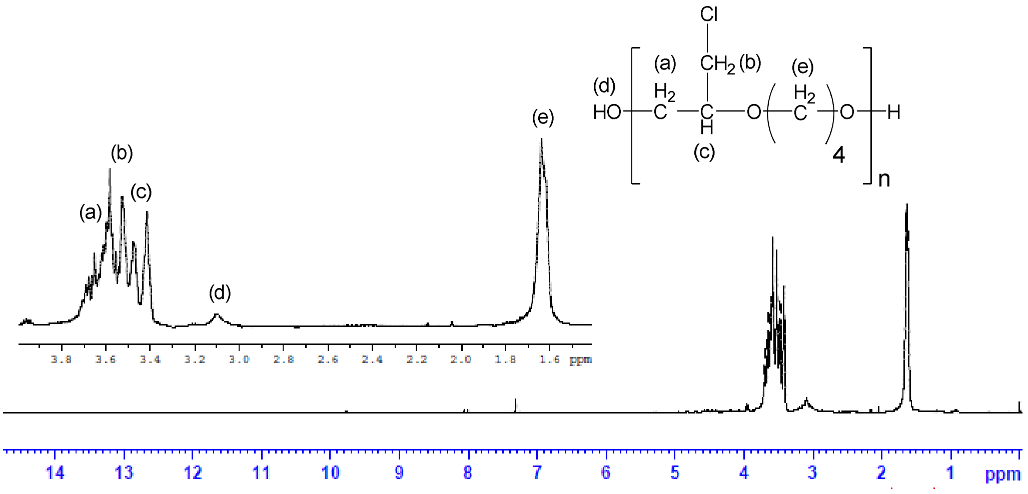


Fig. 2.4:^{1}H NMR spectrum of PECH-diol

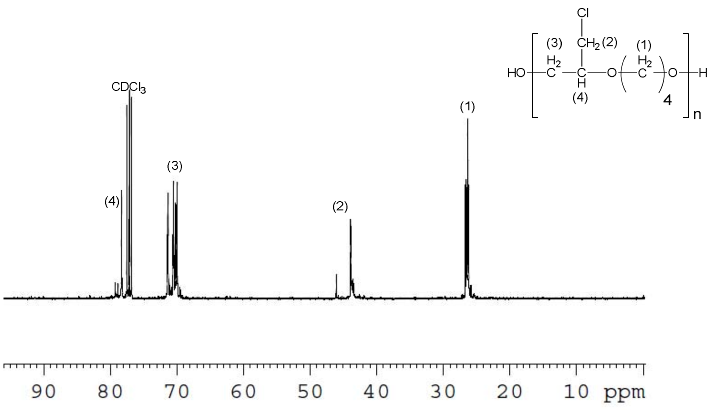


Fig. 2.5:^{13}C NMR spectrum of PECH-diol

The PECH-dioliscolourless, viscous liquid with a glass transition temperature (Tg)below room temperature. The thermal analysis of PECH-diolusing DSC wasperformed and Figure 2.6shows the result. The PECH-diol shows a glasstransition temperature around -39°C, which is in agreement with the literature [9].

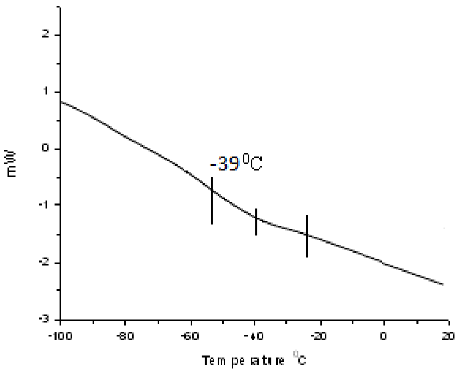
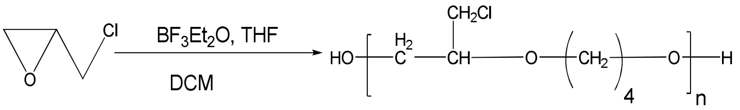


Fig. 2.6: DSC curve of PECHdiol

These results show that polymerization of poly(epichlorohydrin) via cationic ringopeningpolymerization using borontrifluorideetherate(catalyst) and 1,4butanediol(initiator) was successful and reproducible. The yield was about 90% and polydispersity index (1.1). The cationicpolymerization of epichlorohydrin without a diol is reported to yield a wide range ofproducts with varying molecular weights [4, 10].

2.2.2 Synthesis and characterization of PECH-THF diol

The present investigation emphasises on the synthesis and characterization of PECH-THFdiol(polyepichlorohydrin-tetrahydrofuran) diol (Scheme 2.2**)**, synthesized by classical monomer polymerization technique using THF, BF_3Et_2O (borontrifluorideetherate) and ECH (epichlorohydrin) without any low molecular weight polyhydroxy alcohols.



Scheme 2.2 Synthesis of PECH- THF diol

A typical GPCprofile of PECH-diol is shown in Figure 2.7. High yields and narrow molecular weightdistributions (MWD) could be achieved compared to PECH-THF diol.

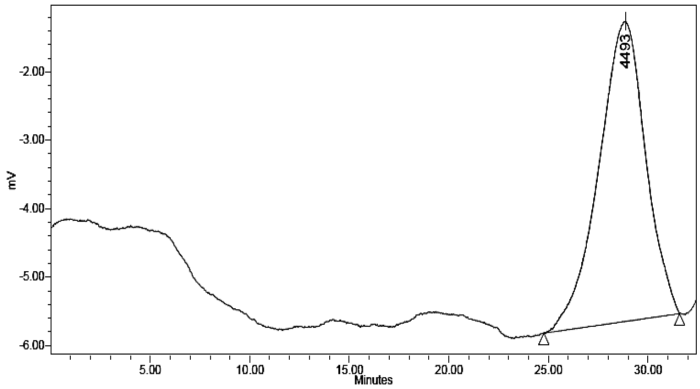


Figure 2.7:GPC trace of PECH-THF diol, Mn = 4493 and polydispersity index 1.3

The PECH-THF diol iscolourless, viscous liquid with a glass transition temperature (Tg)below room temperature. The thermal analysis of PECH-THF diol was carried out using DSC. The PECH-THF diol showed a glasstransition temperature around -37 °C.

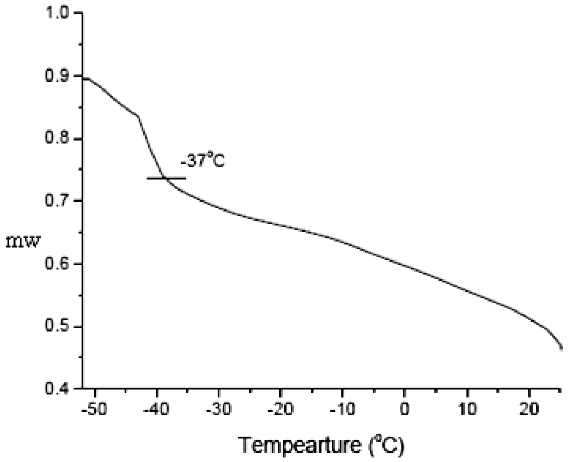


Fig 2.8: DSC curve of PECH-THF diol

The UV-Vis spectrum, IR spectrum, ^{1}H &^{13}C NMR spectra are same as that of PECH diol since the structural pattern is same. High molecular weight and slight change in glass transition temperature is observed for the PECH-THF diol which was synthesized through classical cationic polymerization.

In the study on the effect of THF on the polymerization, in which THF to ECH ratio of 1:2 gave maximum yield with PDI of 1.38. But higher molecular weight and PDI was observed for higher mole ratios of ECH and THF, especially 1:1.

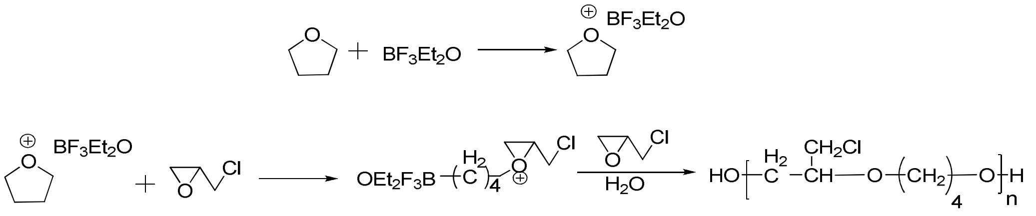
Table 1: Polymerization studies of PECH-THF doils

Sl.No.	Polymer	ECH (mmol)	THF(mmol)	Polymer yield (%)[a]	PECH-THF Molecular Weight by GPC		
					Mn	Mw	PDI[b]
1	PECH-THF diol	10	10	87	4493	5886	1.31
2	PECH-THF diol	10	7.5	91	4450	5696	1.28
3	PECH-THF diol	10	5	95	4463	5579	1.25
4	PECH-THF diol	10	2.5	90	4435	5366	1.21
5	PECH-THF	10	1.25	86	4478	5195	1.16

	diol						
6	PECH-THF diol	10	0.625	78	4430	4962	1.12

[a]Polymer yield= (weight of the polymer/(weight of THF + weight of ECH) x 100;[b]PolydispersityIndex (PDI) = M_w/M_n

The polymerization is believed to occur through the classical cationic polymerization in which the THF forms a complex with BF_3etherate which in turn attacks the ECH and induces the ring opening polymerization (ROP). The polymerization can be terminated by the addition of water and forms the hydroxyl terminated polymer. The end hydroxyl groups present in the polymer is confirmed by characteristic signal in the NMR spectra.



Scheme 2.3: The classical cationic ring-opening polymerization ofepichlorohydrin and THF in the presence of borontrifluorideetherate (catalyst).

2.2.2.1 Effect of using different solvents

The use of either toluene or dichloromethane had very little effect on the product.However, when dichloromethane was used as the solvent, viscosity increased to such an extent thatstirring with a magnetic stirring bar was found to be difficult. If toluene was used as the solvent it was found to be difficult in removing the trace amount of solvent as compared to dichloromethane.

2.2.2.2 Hydroxyl value of the polymer

The polymer was treated with standard acetylating agent comprising of acetic anhydride and pyridine. Each sample containing unreacted acids and blanks were titrated with standard NaOH solution. The difference between sample and blank was used to calculate the hydroxyl value of the copolymer.

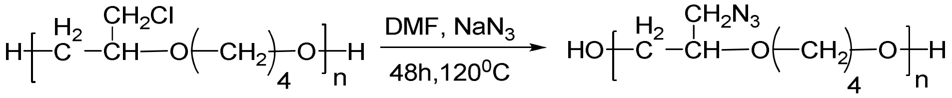
Table 2: Hydroxyl value of PECH diol and PECH-THF diol

Sl. No.	Polymer	Hydroxyl Value (mg KOH/g)
1	PECH diol	62
2	PECH- THF copolymer	83

2.2.3 Synthesis and characterization of poly(glycidylazide-THF)diol

Section 2.2.3 includes results from the synthesis of glycidylazide polymer and estimation of hydroxyl groups in the polymer backbone terminal.

Glycidylazide polymer [45-52] was synthesized by the azidation of PECH-THF diol with sodium azide in DMF at 120^0C. In this study, azidation of PECH-THF proceeded to a high degree of nucleophilic substitution and yielded a polymer with a polydispersityindex (1.38).Scheme 2.4is a representation of thereaction scheme for the azidationof PECH-THF diol.



Scheme 2.4: Synthesis of GAP-THF diol

The density of the GAP-diol was determined using a pyknometer, and found to beabout 1.3 g/ml which is comparable with values reported in the literature [23].

The GPC profile of the GAP-THF diol is shown in Figure 2.9 below. In theazidation reaction of PECH-THF diolwith sodium azide, chlorine was replaced byazide groups, which led to an increase in the molecular weight. Usually, themolecular weight of the GAP-THF diol was higher than the PECH-diol used in theazidation process. This could be attributed to the difference in the nature of azidegroups as opposed to chloromethyl groups (hydrodynamic volume and interactionwith polystyrene stationary phase).In any case, the polydispersity index was not affectedconsiderably by the azidation process. On the other hand, it is reported that highmolecular weight poly(epichlorohydrin) (rubber) or poly(epichlorohydrin-co-ethyleneoxide) azidation reactions lead to a decrease in molecular weight due to degradationof some PECH chains duringazidation reaction. This was not noticed in anyof the experiments carried out in this study.

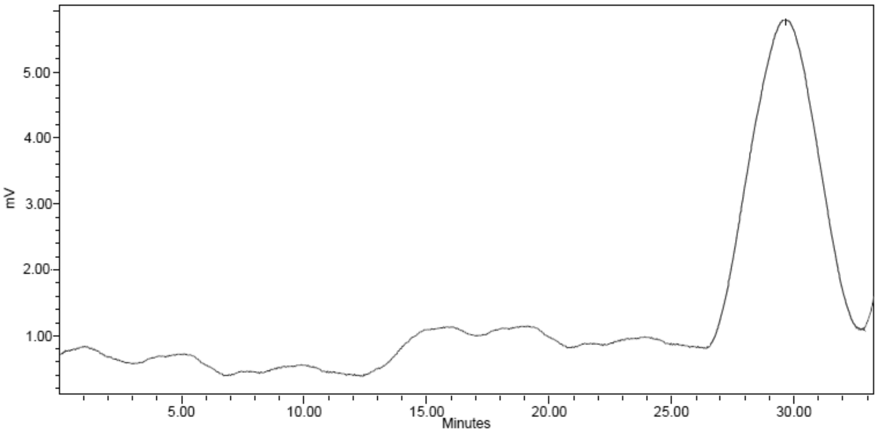


Figure 2.9:GPC trace of GAP-THF diol, Mn = 6228 and polydispersityindex 1.38.

The UV-Vis spectrum of GAP-THF diol is shown in Figure 2.10**.** The UV-Vis spectrum showed absorption peakfor GAP-diolaround300 nm where as UV-Vis spectrum of PECH-THF did not show anyabsorption peak in the 600-

200 nm region, which indicated that theazide group was substituted in the polymer backbone.

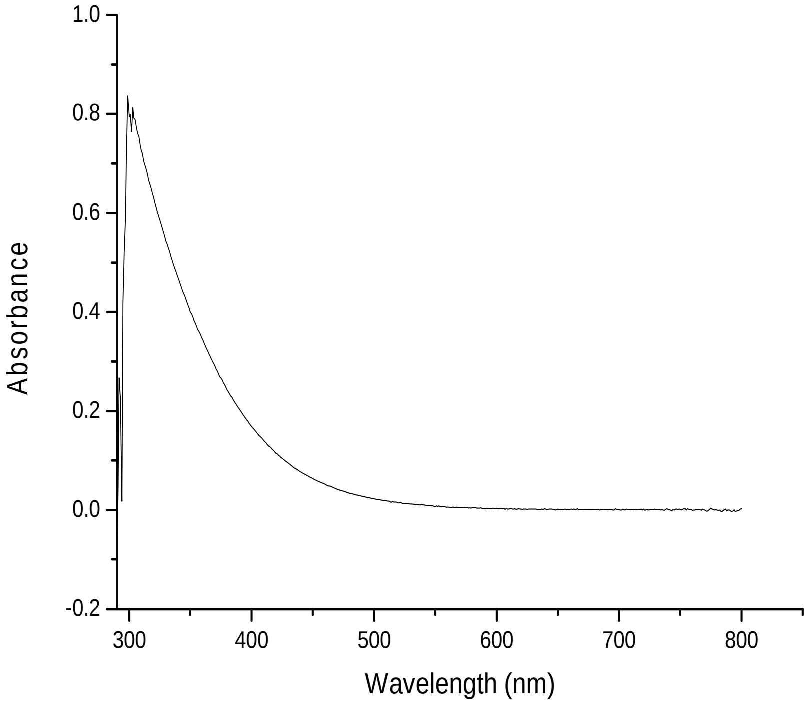


Figure 2.10:UV-Vis spectrum of GAP-THF diol.

The FTIR spectrum of the GAP-diol is shown in Figure 2.11. The importantcharacteristic peaks are the absorption peaks around 1140 and 2100 cm^{-1}, whichcorrespond to the polyether linkage and azide groups, respectively. Absorptionpeaks around 2850 and 3450 cm^{-1} are attributed to the methylene and terminalhydroxyl groups, respectively. In the IR spectrum, the disappearance of the peak around 745 cm^{-1} and the formation of the peak around 2100 cm^{-1}are attributed to thereplacement of chlorine atoms of PECH-diol with the azide groups of GAP-diol. Ithas been reported that the azidation reaction slow down after reaching about 90% conversion[23]. For this reason, it is preferable to carry out the reaction with an excess ofsodiumazide.

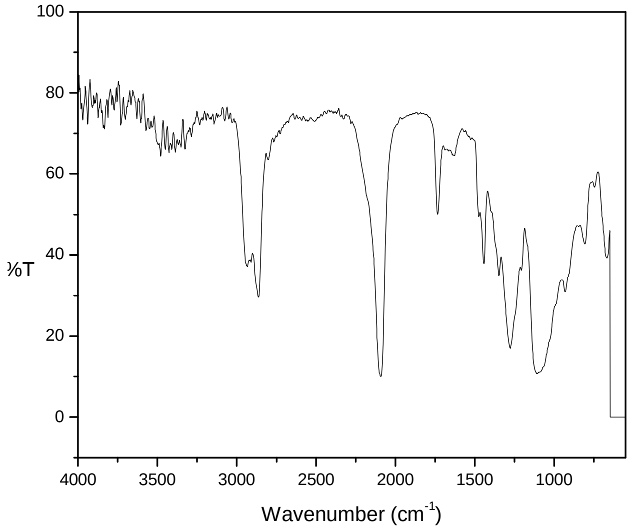


Figure 2.11:FTIR spectrum of GAP-THF diol

The GAP-THF diol was characterized by ^{1}H-NMR, as shown in Figure 2.12. The important feature of this spectrum is the signal around 3.2 ppm, which is assigned tomethylene protons of the pendant azidomethyl groups (CH_2N_3), and the signal around 3.45-3.8 ppm, which is assigned to the main chain methylene and CH protons. The proton NMR spectrum also exhibited a peak at 1.5 ppm due to –CH_2 of THF.

The ^{13}C-NMR spectrum of GAP-THF diol is shown in Figure 2.13. The major assignments on this spectrum are the signal around 50-53 ppm, which is attributed totheazide attached carbon. The absence of a signal around 43-45 ppm, which is associatedwith the chloromethyl group of PECH-diol (see Figure 2.6), means that most of thechlorine atoms located on the chloromethyl pendant groups of PECH have beensubstituted with azide groups. The signal around 69-71 ppm is associated with thepolyether linkage (–O–CH_2–). Solvent peak appears at 77 ppm and the signal around79 ppm is attributed to the (–HO–CH–). The strong resonance peaks of methylene protons of THF in GAP-THF diol were visible around 25 ppm.

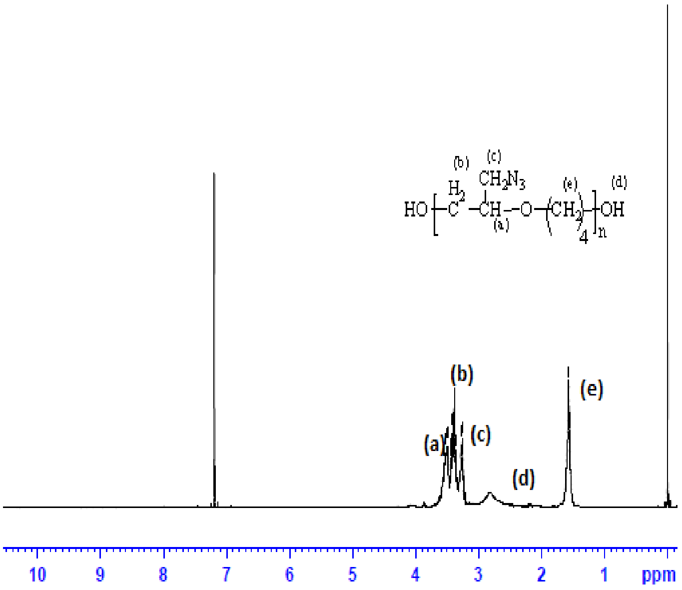


Figure.2.12:^{1}H NMR spectrum of GAP-THF diol

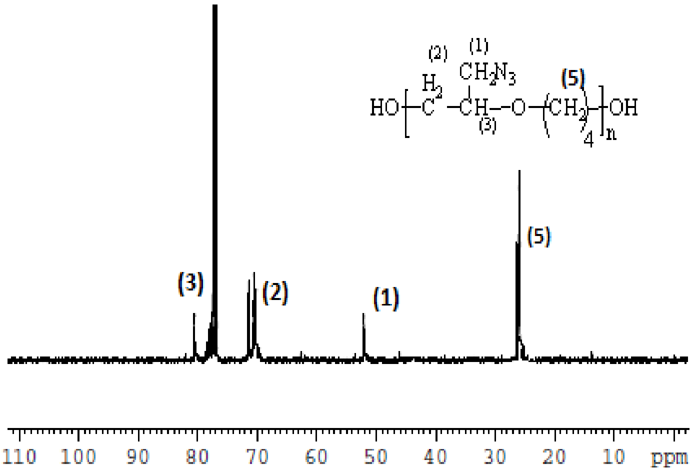


Figure.2.13:^{13}C NMR spectrum of GAP-THF diol

GAP-THF diol wasan amper colored liquid. Thermal behavior at low temperature representsan important feature for polymeric materials used in propellant formulation.Thethermal analysis of GAP-THF diol was performed by DSC and Figure 2.14shows theresults for a low temperature scan. The GAP-THF diol showed glass transition temperature around -35°C.

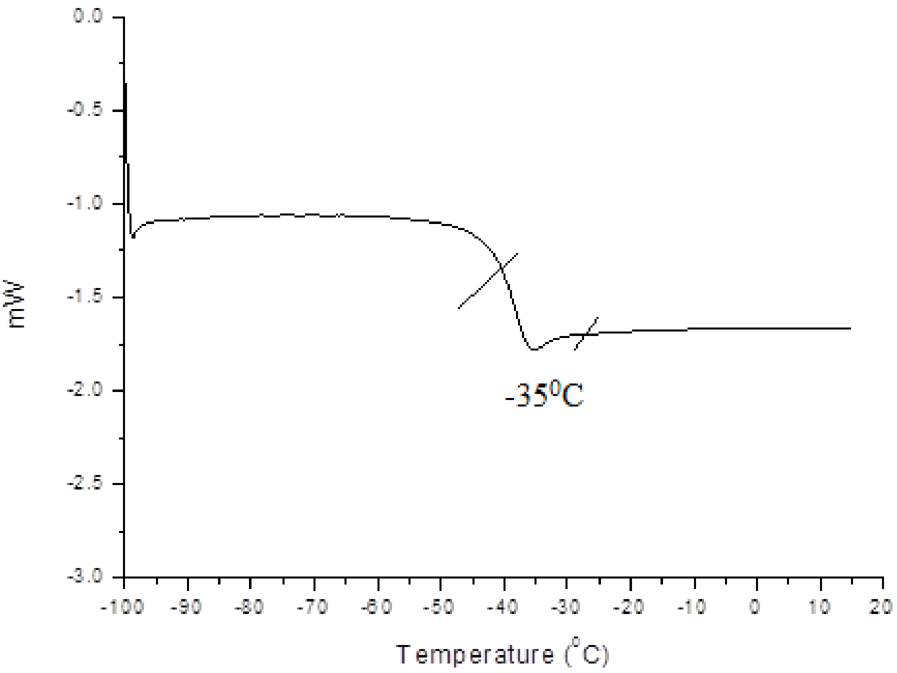


Figure.2.14: DSC curve of GAP-THFdiol

It is essential to study the decomposition behavior of polymeric propellant materials,especially in the case of such materials being used in space technology applications,where thermal decomposition of the propellant binder plays a crucial role in thecombustion of the composite solid propellants. It was therefore necessary to study thethermal decomposition behavior of the GAP-THF diol produced. The decompositiontemperature of the GAP-THF diol was determined from a DSC thermogram at hightemperature. Results are recorded in Figure 2.15. The DSC scan of GAP-THF diol showed an exothermic peak in the temperature range 180-273°C, with the maximum around 248±5°C. The exothermic decomposition was attributed to the scission of the azide bonds from the azide pendant groups of the glycidylazide polymer.

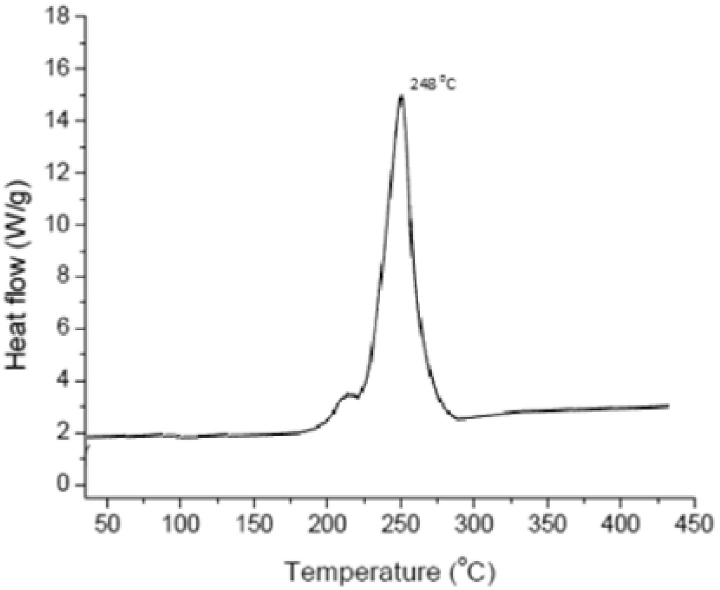


Figure 2.15: DSC thermogram of GAP-THF diol

The polymerization studies were carried out using different mol ratios of THF and maximum yield was obtained in which THF to ECH ratio was 1:2 and with PDI of 1.38. But higher molecular weight and PDI was observed for higher mole ratios of ECH and THF especially 1:1. The results of the polymerization studies are given in the Table 3.

Table 3: Polymerization studies of PECH-THF diol and GAP-THF diol

Sl. No.	Polymer	ECH (mmol)	THF (mmol)	Polymer yield (%)[a]	PECH-THF Molecular Weightby GPC			GAP-THF Molecular Weightby GPC		
					Mn	Mw	PI[b]	Mn	Mw	PDI
1	PECH-THF diol	10	10	87	4493	5886	1.31	6240	8861	1.42
2	PECH-THF diol	10	7.5	91	4450	5696	1.28	6120	8568	1.40
3	PECH-THF diol	10	5	95	4463	5579	1.25	6228	8595	1.38
4	PECH-THF diol	10	2.5	90	4435	5366	1.21	6040	7731	1.28
5	PECH-THF diol	10	1.25	86	4478	5195	1.16	6380	7911	1.24
6	PECH-THF diol	10	0.625	78	4430	4962	1.12	6445	7799	1.21

[a] Polymer yield= (weight of the polymer/(weight of THF + weight of ECH) x 100;[b] PolydispersityIndex (PDI) = M_w/M_n

2.2.3.1 Effect of using different solvents

The use of either DMF or DMSO had a very little effect on the product.However, ease of removal of solvent from the reaction medium was found to be operative when DMF was used as the solvent over DMSO. The use of water as solvent was also studied, but the poor solubility of the polymer, requirement of large amount of phase transfer catalyst and increased reaction time ruled out this method.

2.2.3.2 Effect of using different catalyst

The effect of catalyst on the azidation reactions was checked by varying the amount of NaN_3 to catalyst and using the same solvent and fixed temperature. The reaction was optimized and found that TBAB was the effective catalyst for azidation of PECH-THF diol and maximum yield was obtained for the NaN_3 to TBAB ratio 37:0.1. Table 4presents the effect of catalyst on reaction time.

Table 4: Effect of catalyst on reaction time

Sl. No.	**Polymer PECH-THF (mmol)**	**Catalyst**	**NaN_3/Catalyst mol ratio**	**Solvent**	**Reaction Time(h)**	**Temperature (^0C)**
		LiCl TBAB				
1	12.2	TBAB	74:0.1	DMF	60	120
2	12.2	TBAB	37:0.1	DMF	48	120
3	12.2	TBAB	25:0.5	DMF	48	120
4	12.2	LiCl	74:0.1	DMF	156	120
5	12.2	LiCl	37:0.1	DMF	144	120
6	12.2	LiCl	2.5:0.5	DMF	120	120

2.2.3.3 Hydroxyl value of the polymer

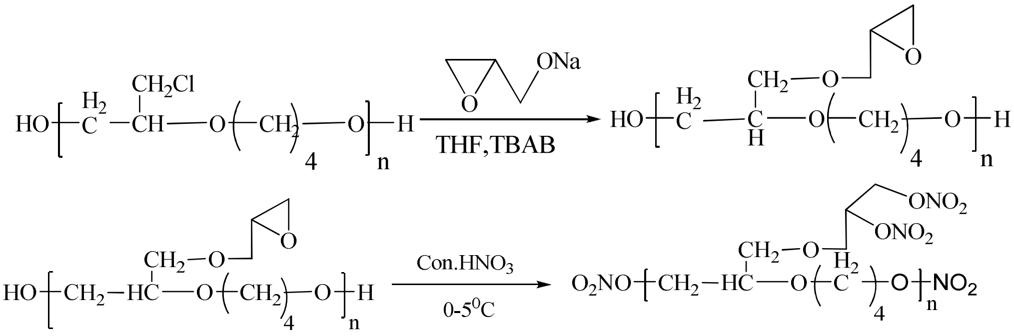
The polymer was treated with standard acetylating agent comprising of acetic anhydride and pyridine. Each sample containing unreacted acids and blanks were titrated with standard NaOH solution. The difference between sample and blank was used to calculate the hydroxyl value of the copolymer. The results are given in Table 5.

Table 5: Hydroxyl value of GAP-THF diol

Sl. No.	Polymer	Hydroxyl Value (mg KOH/g)
1	GAP-THFdiol	62

2.2.4 Synthesis of poly(dinitropropan-1-oxy)oxirane (PDNPO)

Synthesis of the polymer PDNPO was done in two steps.First step was the substitution of sodium salt of glycidol in the precursor PECH-THFdiol followed by nitration using 90% HNO_3. In this study, substitution of PECH-THF followed by nitration yielded a polymer with a polydispersity index (1.3).



Scheme 2.5: Synthetic route to the polymerPDNPO

The density of the PDNPO was determined using a pyknometer, and was found to be1.2 g/ml.

The GPC profile of the PDNPO is shown in Figure 2.16. In the nitration reaction, the glycidol was ring opened and got nitrated, which led to an increase in the molecular weight.The number average molecular weight was found out using GPC and it was found to be 5124 with polydispersityindex 1.3.

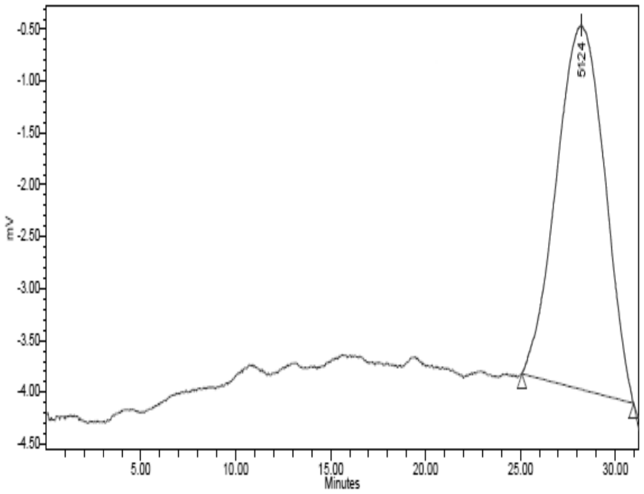


Figure 2.16:GPC trace of PDNPO, Mn= 5124 and polydispersity index 1.3.

The UV-Vis spectrum is shown in Figure 2.17. The UV-Vis spectrum shows absorption peakfor PDNPOaround450 nm. This absorption could be attributed to the nitratogroup, it was not observed in the UV-Vis spectrum of PECH-THF diol.

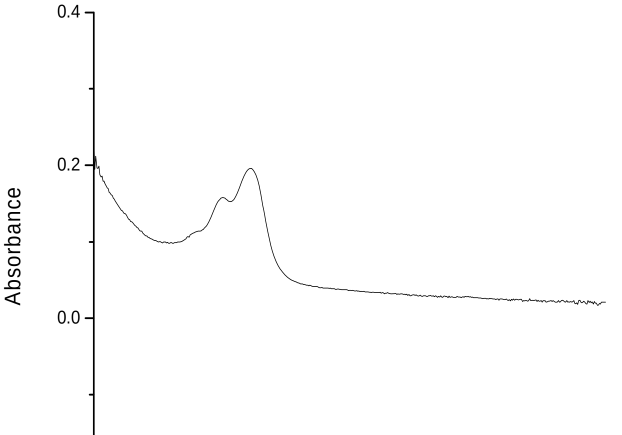


Figure 2.17:UV-Vis spectrum of PDNPO.

The FTIR spectrum of the PDNPO is shown in Figure 2.18. The importantcharacteristic peaks are the absorption peaks around 1140, 1634 and 1277 cm^{-1}, which corresponded to the polyether linkage andnitrato group asymmetric and symmetric stretching vibrations, respectively. Absorptionpeaks around 2850 cm^{-1}was attributed to the methylene group. The peak at 3450 cm^{-1} was found to disappear and it would be due to the complete nitration including the terminal hydroxyl groups, since 90% HNO_3 was used. In the IR spectrum, the disappearance of the peak around 745 cm^{-1} and the formation of the peak around1634 and 1277 cm $^{-1}$, were attributed to the replacement of chlorine by nitrato groups.

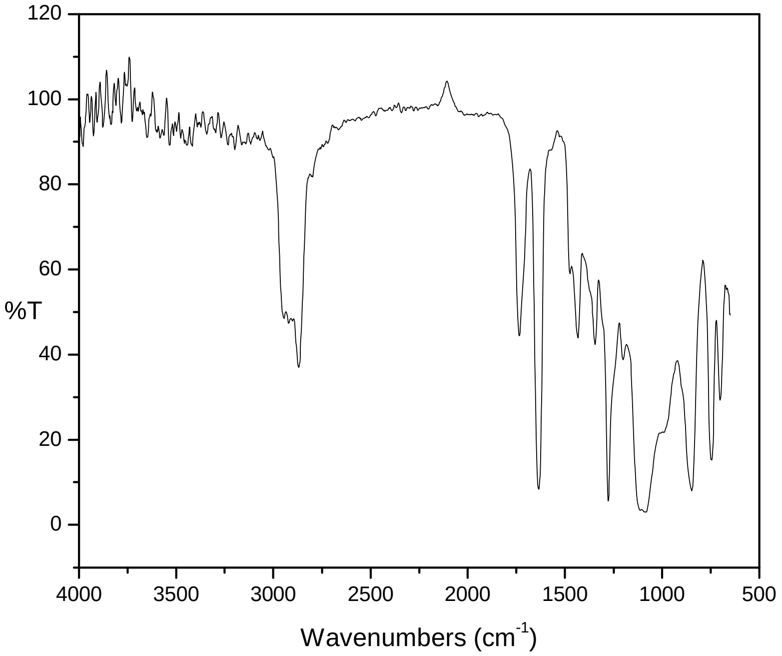


Figure 2.18:FTIR spectrum of PDNPO

The important features of the ^{1}H NMR spectrum (Fig.2.19) are the signals at 5.5 ppm, as multiplet which correspond to the -CH_2 protons in -CH_2ONO_2, 3.8 ppm due to –OCH_2 protons, 3.5 ppm –CH protons and at 1.5

ppm of –CH$_2$protons of THF respectively. The proton NMR spectrum also exhibited a peak at 1.5 ppm due to –CH$_2$ of THF.

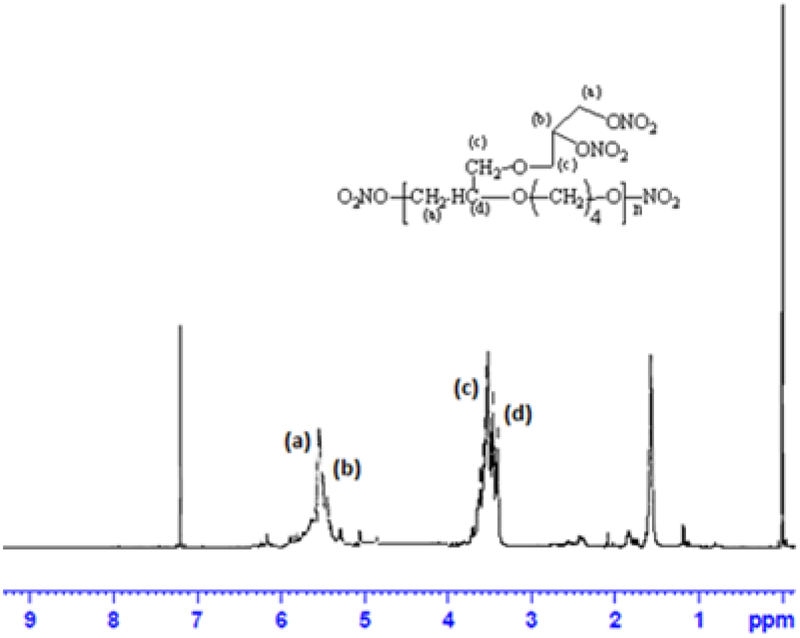


Figure2.19:^{1}H NMR spectrum of PDNPO

The ^{13}C-NMR spectrum of PDNPO is shown in Figure 2.20. The importantassignment on this spectrum is the signal around 92-95 ppm, which is attributed tothenitrato group attached carbon. The absence of a signal around 43-45 ppm, which is associatedwith the chloromethyl group of PECH-THF diol (Figure 2.6), means that most of thechlorine of the chloromethyl pendant groups of PECH have been fully substituted. The signal around 69-71ppm is associated with thepolyether linkage (–O–CH$_2$–). The signal around 70-74 ppm is associated to the group (–O–CH$_2$–CH-).Solvent peak appears at 77 ppm, the signal around 93 ppm is attributed to the (–CH–ONO$_2$)and the signal around 79 ppm is attributed to the (–HO–CH–). The strong resonance peaks of methylene protons of THF in PDNPO were visible around 25 ppm.

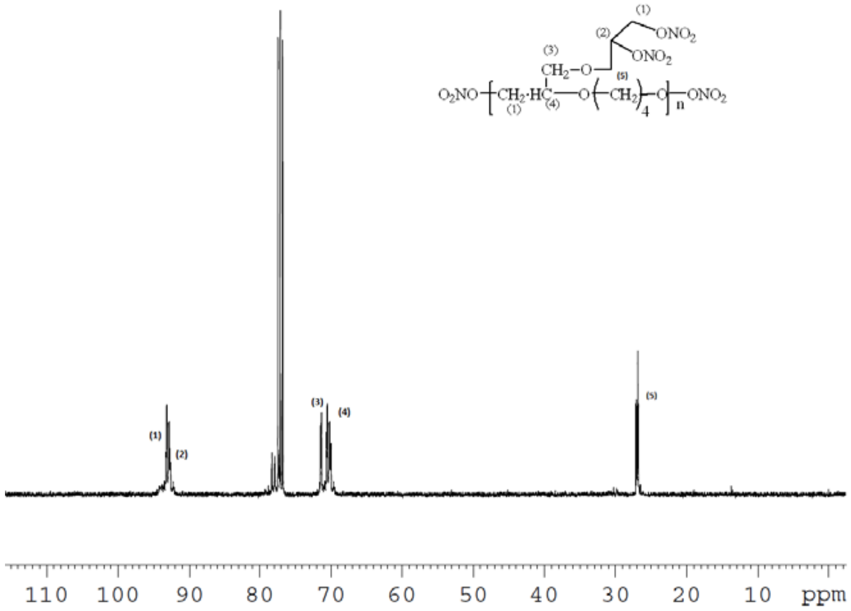


Figure 2.20:^{13}C NMR spectrum of PDNPO

PDNPO was an yellow viscous liquid with a glass transition temperature below room temperature. The thermal analysis of PDNPO using DSC (Fig.2.21) was performed and the glass transition temperature was found to be -38 ^{0}C.

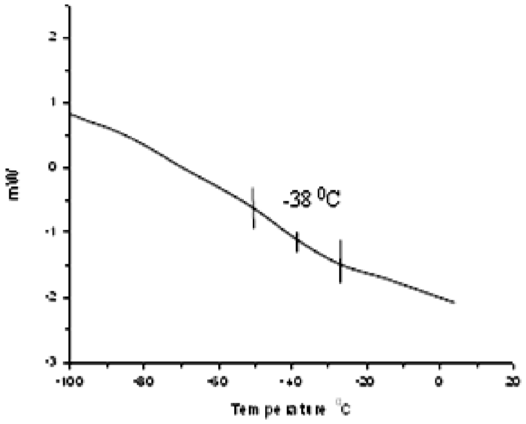


Figure 2.21:DSC curve of PDNPO

The evaluation of the thermal stability of energetic polymers is vital since it decides whetherthe polymers are suitable for use in energetic formulation [53-57]. It was therefore necessary to study thethermal decomposition behavior of PDNPO produced. The decompositiontemperature of PDNPO was determined from a DSC thermogram at hightemperature. Results are recorded in Figure 2.22. The DSC scan of PDNPO shows asingle exothermic peak in the temperature range 160-240°C, with the maximumofthepeakaround 210±5°C. This result is in agreement with the literatureand the exothermic decomposition is attributed to the elimination of -ONO_2 by thescission of the -ONO_2 bonds from the nitrato pendant groups of the PDNPO.

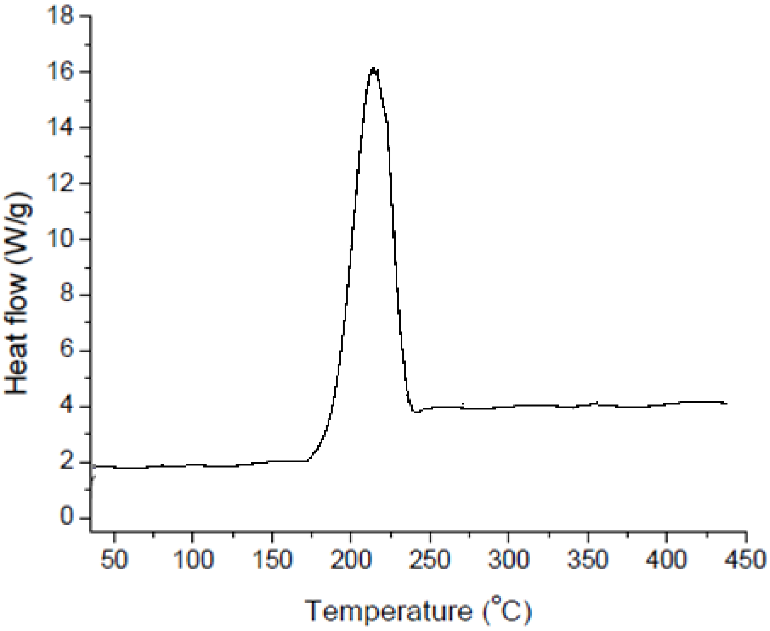


Figure 2.22:DSC thermogram of PDNPO

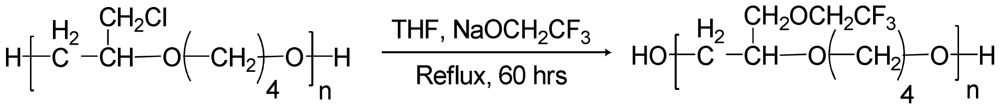
The effect of catalyst and substituent on the synthesis of PDNPO was studied by varying the amount of substituent and catalysts. It was found that, the maximum yield was obtained in the case where the sodium glycidate and PECH-THF diol in the ratio (1.5:1) and for that 0.122 mmol of TBAB was used. The effect of substituent and catalyst on the synthesis of PDNPO is shown below (Table 6).

Table6: Effect of catalyst and substituent on the synthesis of PDNPO

Sl.No.	Polymer (PECH-THF diol) mmol	Sodium salt of Glycidol (mmol)	Catalyst (TBAB) (mmol)	Polymer yield (%)	Reaction Time (h)
1	6.1	6.1	0.122	68	48
2	6.1	6.1	0.061	67	48
3	6.1	12.2	0.122	70	48
4	6.1	9.15	0.122	72	48

2.2.5 Synthesis and characterization of poly(bistrifluoroethoxy)diol (PBTEO)

PBTEO diol polymer was synthesized by the substitution of sodium salt of trifluoroethanol in dark under reflux in THF for 60 h. In this study, nucleophilic substitution of sodium trifluoroethanolate yielded PBTEO polymer with a polydispersity index of 1.4.Scheme 2.6is a representation of thereaction scheme for the substitution of trifluoroethoxy group on PECH-THF diol.



Scheme 2.6: Synthesis of PBTEO diol

The density of the PBTEO diol was determined using a pyknometer, and found to beabout 1.8 g/ml.

The GPC profile of the PBTEO diol is shown in Figure 2.23. The substitution reaction of PECH-THF diol with trifluoroethanolleads to an increase in the molecular weight.The number average molecular weight was found out using GPC and it was found to be 6580 with polydispersityindex 1.48.

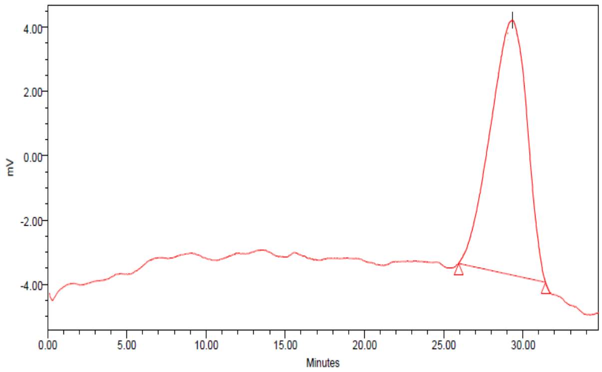


Figure 2.23:GPC trace of PBTEO diol, Mn = 6580 and polydispersity index 1.48.

The FTIR spectrum of the PBTEO diol is shown in Figure 2.24. The importantcharacteristic peaks are the absorption peaks around 1100 and 1350 cm^{-1}, whichcorrespond to the polyether linkage and CF$_3$groups, respectively. Absorptionpeaks around 2850 and 3450 cm^{-1} are attributed to the methylene and terminalhydroxyl groups, respectively. In the IR spectrum, the disappearance of the peak at 745 cm^{-1} and the formation of the peak at 1120 cm^{-1}, are attributed to the replacement of chlorine of the PECH-THF diol with –OCH$_2$CF$_3$ groups.

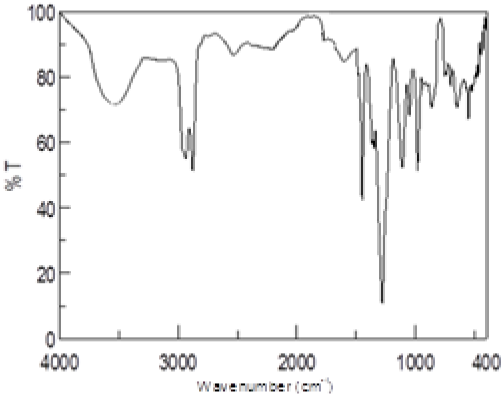


Figure 2.24:FTIR spectrum of PBTEO diol

The polymer was characterized by ^{1}H-NMR spectrum, as shown in Figure 2.25. The important feature of this spectrum is the signal at 4.5 ppm, which is assigned tomethylene protons of the -CH_2CF_3 group, and the signal around 3.45-3.8 ppm, which is assigned to the main chain methylene andCH protons. The proton NMR spectrum also exhibited a peak at 1.5 ppm for –CH_2 of THF. The terminal –OH group showed a signal at 3.1 ppm.

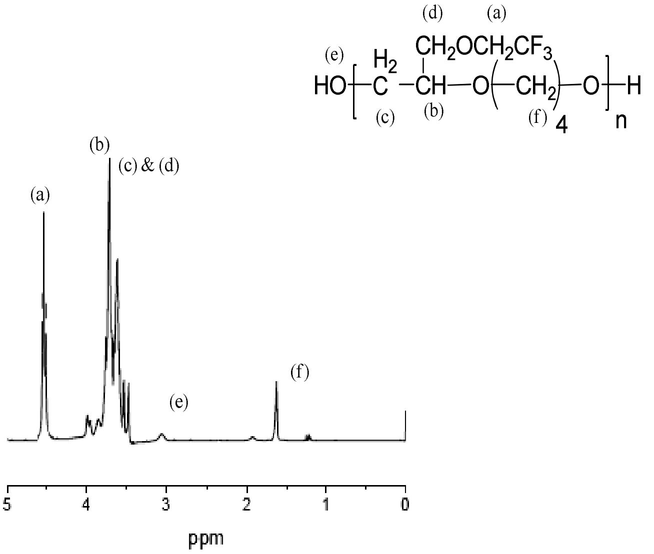


Figure 2.25:^{1}H NMR spectrum of PBTEO diol

The ^{13}C-NMR spectrum of PBTEO diolis shown in Figure 2.26. The importantassignment on this spectrum is the signal around 61-63 ppm, which is attributed tothe -CH_2 of the –CH_2CF_3 groups. The absence of a signal around 43-45 ppm, which was associated with the chloromethyl group of PECH-diol (see Figure 2.6), means that most of thechlorine of the chloromethyl pendant groups of PECH have beensubstituted with –CH_2CF_3 groups. The signal at 123 ppm which appears as a quartet is attributed to the –CF_3 carbon atom of the –CH_2CF_3. The signal around 69-71ppm is associated with thepolyether linkage (–O–CH_2–). Solvent peak appears at 77 ppm and the signal at 79 ppm is attributed to the (–HO–CH–). The strong resonance peaks of methylene protons of THF in PBTEO–diol were visible around 25 ppm.

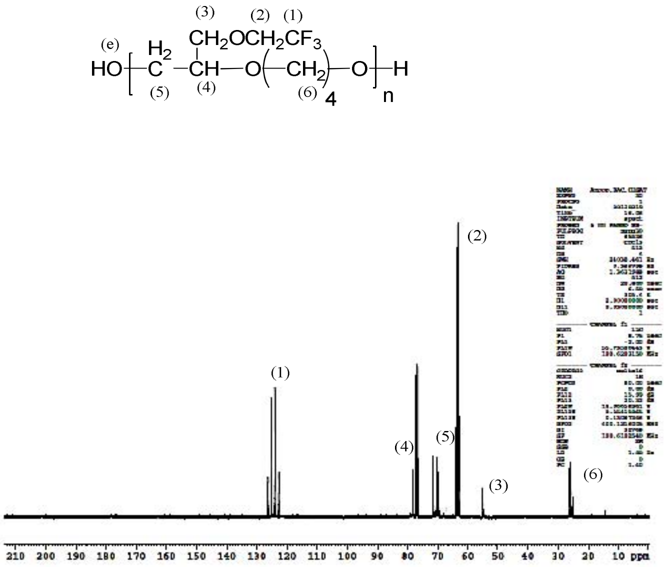


Figure 2.26: The ^{13}C-NMR spectrum of PBTEO diol

PBTEO diol was a pale yellow coloured liquid. Thermal behavior at low temperature representsan important feature for polymeric materials used in propellant formulation.Thethermal analysis of PBTEO diol was performed by DSC and Figure 2.27shows theresults for a low temperature scan. The PBTEO diol showed glass transition temperature around -49°C, which is suitable for binder applications.

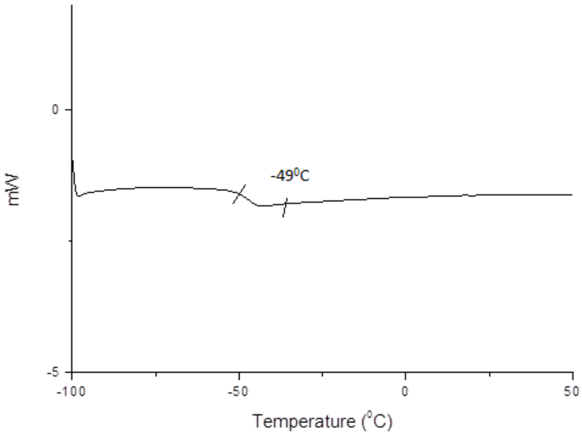


Figure 2.27:DSC curve of PBTEO diol

The decompositiontemperature of the PBTEO diol was determined from a DSC thermogram at hightemperature. Results are recorded in Figure 2.28. The DSC scan of PBTEO diol shows single exothermic peak in the temperature range 310-360°C, with the maximum of the peak around 340±5°C.The exothermic decomposition is attributed to the scission of the CF_3 bonds from the $–CH_2CF_3$ groups of the PBTEO diol.

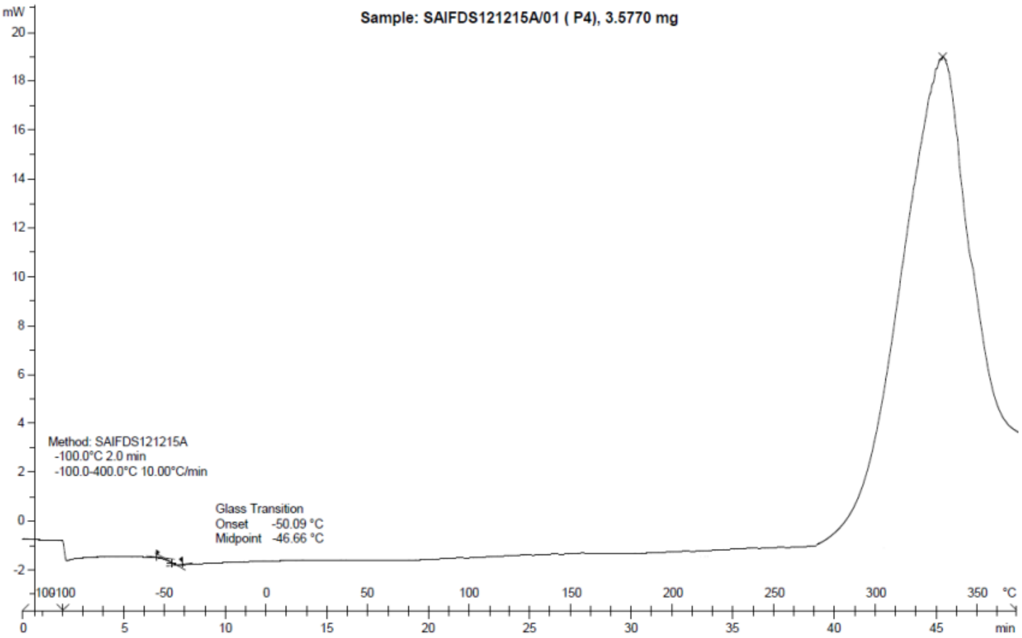


Figure 2.28:DSC thermogram of PBTEO diol

The effect of catalyst and the substituent on the synthesis of PBTEO diol was studied by varying the amount of substituent and catalysts. It was found that the maximum yield was obtained in the case where 1.2 times of the substituent (7.32 mmol) has been used against the polymer amount (6.1 mmol) and where 0.122 mmol of TBAB was used. The effect of substituent and catalyst on the synthesis of PBTEO diol is shown in Table 7.

Table 7: Effect of substituent and catalyst on the synthesis of PBTEO diol

Sl.No.	Polymer (PECH-THF diol) (mmol)	Sodium trifluoroethanolate (mmol)	Catalyst (TBAB) (mmol)	Polymer yield (%)	Reaction Time (h)
1	6.1	6.1	0.122	52	72
2	6.1	6.1	0.061	55	72
3	6.1	12.2	1.22	64	72
4	6.1	7.32	1.22	72	60

2.2.5.1 Hydroxyl value of the polymer

The polymer was treated with standard acetylating agent comprising of acetic anhydride and pyridine. Each sample containing unreacted acids and blanks were titrated with standard NaOH solution. The difference between sample and blank was used to calculate the hydroxyl value of the copolymer. The results are given in TABLE 8.

Table 8: Hydroxyl value of PBTEO diol

Sl. No.	Polymer	Hydroxyl Value (mg KOH/g)
1	PBTEO diol	58

2.3 Conclusion

The main objective of this part of the study was achieved by applying cationic ringopeningpolymerization of ECH monomers in reactions, using low molecular weightdiol as initiator and BF_3etherate as catalyst to yield PECHdiol and PECH-THF diol copolymer. The products werecharacterized using different characterization techniques such as GPC, UV-Vis, FTIR,proton and carbon NMR, and DSC. The molecular weight of the polymer was found to be 2224 and 4439 and thepolydispersityindex 1.1 and 1.3 respectively, based on polystyrenestandards. The thermal analysis using DSC showed glass transition temperature in the range (-40 to -35^{o}C). The nature of PECH-diolendgroups have been studied after esterification reaction of hydroxyl groups with standard acetylating agent. Effect of different solvents on the product has been investigated. We have optimized the polymerization reaction using different mole ratios of the THF and keeping the ECH amount constant and observed significant difference in the polymerization yield and product properties such asmolecular weight and polydispersityindex. Thus PECH diol was successfullyproduced and was utilized in the next phase of the study.

The synthesis and characterization of glycidylazidepolymer was also discussed here. This polymer was prepared by the azidationreactionof PECH-THF copolymer. The GAP-THF diol had molecular weight (M_n) of 6000-9000 and polydispersity index of 1.3-1.4, asdetermined by GPC. The polymer was characterized by UV-Vis, FT-IR and NMR spectroscopic technique which confirmed the structure of the polymer. Thermal analysis of the polymer was studied byDSC. It showed a glass transition temperature at -35°C and thedecomposition took place around 248 °C. The polymer PDNPO was prepared by the nucleophilic substitution of sodium salt of glycidol on the PECH-THF copolymer followed by the nitration with 90% HNO_3. The polymer formed had a molecular weight (M_n)in the range 5000- 6000 with a polydispersityindex of 1.3 and a glass transition temperature at -38°C.Thermal decomposition of the polymer took place at 210°C and confirmed with DSC. The polymer PBTEO diol was prepared by the substitution of sodium salt of trifluoroethanol on the PECH-THF copolymer.

The polymer formed had a molecular weight (M_n)in the range 6000- 7000 with a polydispersityindex of 1.4. The presence of trifluoroethanol group was confirmed by FT-IR spectroscopy which showed absorption peak at 1350 cm $^{-1}$. The proton and carbon NMR spectroscopy techniques were used to confirm the structure of PBTEO diol. Thermal analysis of the polymer was studied by DSC.

The glass transition temperature was around -49 ^{o}C and thedecomposition took place around340 ^{o}C for the polymer PBTEO.

2.4 Experimental

2.4.1 Synthesis of PECH diol

To a dry 250-mL three-necked, round-bottom flask, placed in a temperaturecontrolled water bath, fitted with a condenser with a calcium chloride guard tube inthe top, and an efficient magnetic stirrer bar, 1.8 ml of 1,4-butanediol (0.02mol) dissolved in 20 mL ofpolymerization solvent (either toluene or dichloromethane) was added. The reaction mixture was stirred for about 15 min in order to ensure homogeneity of the mixture. 5.0 ml borontrifluorideetherate(0.04mol) was added, using a dropping funnel. The reaction mixture changed from a clear, colorless liquid, into a cloudy, white liquid. The reaction mixturewas stirred for another 1 h. To this mixture, 12.5 ml of ECH (0.16 mol) dissolved in 20 mL ofpolymerization solvent was added drop wise over a period of 1h using adropping funnel. The reaction was carried out at room temperature for 3 h before beingquenched by adding 50 mL of distilled water and vigorously stirring for about 30 min.The polymerization was terminated by adding distilled water and vigorously stirring for about 30 min.The crude reaction product was transferred to a separatingfunnel and the organic layer was washed three times with distilled water in order to remove all un-reacted monomer, diol, and borontrifluoride. The organic layer was transferred to around-bottom flask and dried over magnesium sulphate. Finally, the organic layer andproduct was filtered and the solvent was removed by vacuum distillation. In order toremove the solvent, vacuum drying was applied to the product. The polymer was further purified by precipitation from methanol using small quantity of dichloromethane. Theyield was found to be about 90%.

2.4.2 Synthesis of PECH-THF diol

A mixture of 0.82 ml of THF (10 mmol) and 100 ml dichloromethane was added to a 50 ml 3 necked RB flask equipped with a temperature controlled water bath, fitted with a condenser with calcium chloride guard tube in the top, nitrogen inlet and a magnetic stirrer bar. The mixture was allowed to stir for 30 minutes. To this mixture,0.5 ml (4mmol) borontrifluorideetherate wasadded, using a dropping funnel and the mixture was cooled to 0to 5 ^{0}C for 1 h. To this mixture, 0.78 ml (10 mmol) of ECH dissolved in 10 ml of solvent was added drop wise over a period of 1h using a dropping funnel. Exothermic reactions occurred during ring opening process and the ice-salt mixture was removed after 1h. The resulting mixture was warmed to ambient temperature to ensure the completion of the reaction. The polymerization was terminated by adding distilled water (4 mmol) and vigorously stirring for about 30 min. The crude reaction product was transferred to a separating funnel and the organic layer was washed three times with distilled water in order to remove all unreacted monomer, THF and catalyst. The organic layer was transferred to a round-bottom flask and dried over magnesium sulfate. Finally, the organic layer and product was filtered and the solvent was removed by vacuum distillation. In order to remove the solvent, vacuum drying was applied to the product. The polymer was further purified by precipitation from methanol using small quantity of dichloromethane. The yield was found to be about 70%.

2.4.3 Synthesis of GAP-THF diol

Synthesis of the GAP-THF diol was based on the azidation reaction of the precursor PECH-THF, using sodium azide salt and DMF as solvent. In a typical experiment, a clean and dry 250 mL two necked round-bottom flask, immersed in an oil bath at room temperature, was connected to a condenser with a calcium chloride guard tube on the top,a dropping funnel and with magnetic stirrer bar was used in the preparation of GAP. PECH-THF (2 g) (12.2 mmol) was dissolved in dimethylformamide (5 mL) and introduced into the flask. The reaction mixture was heated slowly until the polymer was dissolved in the solvent.About 0.378g of NaN_3 (37mmol) was transferred in small portions within ½ an hour and TBAB 0.039g (0.1mmol) was also added to the reaction mixture.The mixture was heated for 48 h at 120^0C. The polymer solution was diluted to twice the volume of DMF with dichloromethane. The mixture was filtered to separate the unreacted sodium azide and the formed sodium chloride. The dichloromethane solution was removed under vacuum and the resulting viscous liquid was transferred to a separating funnel and washed several times with hot water to remove traces of DMF. Two layers appeared in the separation funnel and dichloromethanewas added to extract the polymer. A solution of polymer in dichloromethane was dried over magnesium sulfate and the pure polymer was obtained by removing the solvent by rotary evaporator. The polymer formed was an ampercolored viscous liquid with yield 75%.

2.4.4 Synthesis of poly(dinitropropan-1-oxy)oxirane (PDNPO)

To a stirred solution of NaH 2.2 g (24.4 mmol) in THF, 6.8 g (9.15 mmol) of Glycidol dissolved in tetrahydrofuran was added over a period of 1h. A solution of PECH-THF (1g, 6.1mmol) in THF was added after 3h. The reaction mixture was heated to reflux in the dark for 3 days in the presence of tetrabutylammonium bromide (0.040 g, 0.122 mmol) phase transfer catalyst. The reaction mixture was cooled, filtered and the solvent was removed under vacuum.5ml concentrated nitric acid (95%) taken in round bottom flask was cooled to 0^0C and glycidol substituted PECH in dichloromethane was added drop wise. The mixture was stirred for 15 minutes, during the reaction the temperature was maintained at 0 to 5^oC. The reaction mixture was poured into ice cold distilled water and dried under vacuum. Yield was found to be 60%.

2.7.5Synthesis and characterization of poly(bistrifluoroethoxy) oxiranediol

To a stirred solution of NaH,(1.1 g,12.2 mmol) in THF, (0.81 g,9.15 mmol) of trifluoroethanol dissolved in tetrahydrofuran was added over a period of 1h. A solution of PECH-THF diol(1g,6.1mmol) in THF was added after 3h. The reaction mixture was heated to reflux in the dark for 60 h in the presence of tetrabutylammonium bromide (0.040 g, 0.122 mmol) phase transfer catalyst. The reaction mixture was cooled, filtered and the solvent was removed under vacuum.The product was washed with distilled waterand the product was dried under vacuum. Yield was found to be 72%.

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Chapter 3

SYNTHESIS AND CHARACTERIZATION OF COPOLYMERS OF OXETANES AND OXIRANES

Abstract

Energetic Thermoplastic Elastomers (ETPE's) have wide range of applications as novel materials for binder application in insensitive munitions and rocket propellants. They form three dimensional networks which absorb and dissipate energy from hazardous stimuli. Advantage of the ETPE is that, it comprises of both soft and hard segments, which will maintain the mechanical properties of the polymeric binder and these are recyclable. BAMO-GLYN copolymer was prepared by the ring opening polymerization using borontrifluoride etherate (BF_3-etherate) as catalyst and 1, 4-butanediol as initiator in which polyBAMO region serves as hard segment and polyGLYN part as soft segment. The copolymer BAMO-NMMO was also synthesized by the copolymerization reaction between BAMO (hard segment) and NMMO (soft segment). GAP-BAMO copolymer was synthesized in two step process. Firstly, poly(epichlorohydrin)-THF copolymer was prepared by the classical cationic ring opening polymerization between Epichlorohydrin (ECH), THF and Bischloromethyl oxetane (BCMO) and in the second step, azidation was done in DMF with sodium azide. The copolymers obtained were characterized using different analytical techniques. Conversion of the chloromethyl groups to azide groups and formation of copolymers were confirmed using FTIR and NMR spectroscopy. Thermal analysis using DSC showed a glass transition temperature of -62 ^{0}C, -86 ^{0}C and -42 ^{0}C for BAMO-GLYN, BAMO-NMMO and GAP-BAMO copolymers with major exothermic decomposition at 242 ^{o}C and 210 ^{0}C. The terminal hydroxyl groups of the polymers were estimated by acetylating them using acetic anhydride and pyridine and analysing the remaining acid by titration.

Keywords: *Thermoplastic Elastomers, PolyBAMO, Glycidyl azide polymer, Oxiranes and Oxetanes.*

3.1 Introduction

Modern solid explosive compositions [1] like propellants, generally consist of particulate solids such as fuel material (metal powders), oxidizers and explosives, which are held together by an elastomeric binder matrix. In this binder matrix the energetic solid [5] filler composition is embedded and immobilized to achieve desired combustion characteristics and also to keep the propellant in a fixed geometry. Conventional binder systems consist of liquid prepolymers that are crosslinked by chemical curing agents. These systems have to be cast within a short time frame after adding the curative, which sets some restriction for the industrial processing. Additionally, the once cured binder material cannot be reused or recycled because, the curing reaction is irreversible.

Energetic thermoplastic elastomers [2-4] provide one possibility to overcome all these disadvantages. Thermoplastic elastomers are block copolymers that exhibit rubber-like elasticity without requiring chemical crosslinking, which present ABA, AB, or (AB)n structure, where A and B are the hard and soft segments respectively. The hard segment (glassy or semi crystalline at room temperature) gives its thermoplastic behavior, whereas the soft segment (rubbery at room temperature) gives the elastomeric behavior [6-10]. Thermoplastic behavior [11-24] results from the formation of rigid domains by chain association due to reversible interaction such as dipole-dipole interactions, hydrogen bonding etc. The soft segments are incompatible with hard segments, hence leading to a microphase separation. Therefore, a thermoplastic elastomer behaves like a rubber because it is crosslinked in the same manner as conventional elastomer, but with reversible physical crosslinks [25-33], instead of chemical ones. For explosive formulations, these elastomers are amenable to injection moulding or twin screw extrusion.

3.2 Results and Discussion

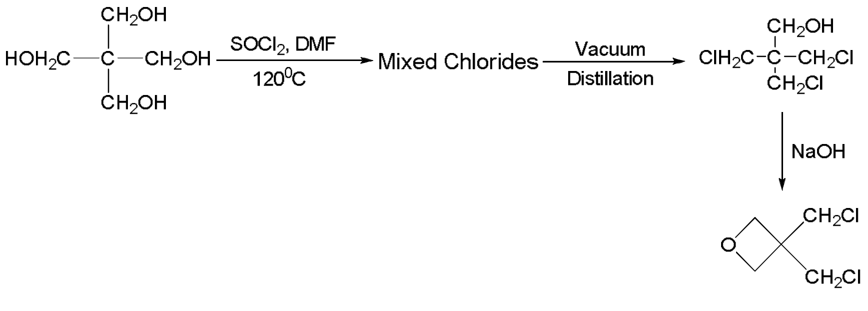
This section discusses the results obtained from the synthesis and characterization of BAMO-GLYN copolymer, BAMO-NMMO copolymer and GAP-BAMO copolymer. The estimation of hydroxyl groups in the polymer backbone terminal is also discussed.

3.2.1 BAMO-GLYN copolymer

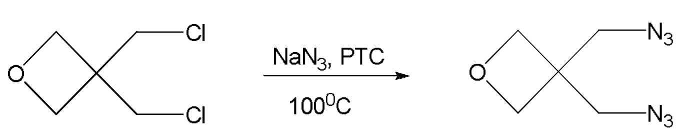
BAMO-GLYN copolymer was synthesized from the copolymerization reaction between BAMO and GLYN using BF_3Et_2O as catalyst and 1,4-butanediol as initiator.

3.2.1.1 Synthesis of BAMO

BAMO was synthesized as per reported methods in which azidation of BCMO (Bischloromethyl oxetane) with NaN_3 was done in the presence of catalyst, where BCMO was synthesized from pentaerythritol using Vilsmeier reagent followed by cyclisation with NaOH. Yield was found to be 56% and 85% respectively for BCMO and BAMO.



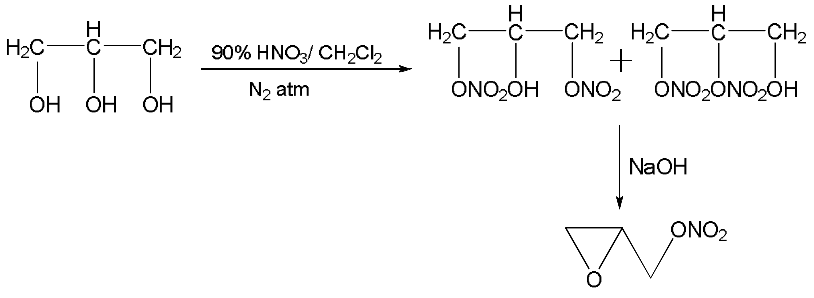
Scheme 3.1: Synthesis of BCMO



Scheme 3.2: Synthesis of BAMO

3.2.1.2 Synthesis of GLYN

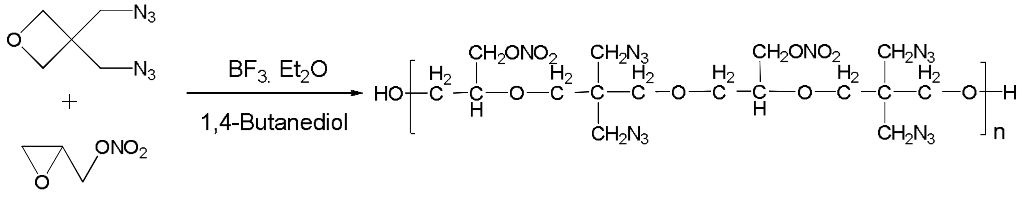
GLYN monomer was synthesized from glycerine by nitration using 90% HNO_3. The nitration products comprising of both 1,3-dinitroglycerine and 1,2-dinitroglycerine were subjected to cyclisation with NaOH. The yield was found to be 70%.



Scheme 3.3: Synthesis of GLYN

3.2.1.3 Synthesis of BAMO-GLYN

BAMO-GLYN polymer was synthesized from the copolymerization reaction between BAMO and GLYN using BF_3Et_2O as catalyst and 1,4-butanediol as initiator. The polymerization of BAMO was initiated through activated monomer polymerization followed by the addition of GLYN monomer to the reaction mixture and terminated by the addition of saturated brine solution.



Scheme 3.4: Synthesis of BAMO-GLYN copolymer

The density of the BAMO-GLYN copolymer was found out by using a pyknometer, and found to be1.3 g/ml.

The GPC profile of the BAMO-GLYN copolymer is shown in Figure 3.1. The number average molecular weight was found out using GPC and it was found to be 2612 with polydispersity index 1.15.

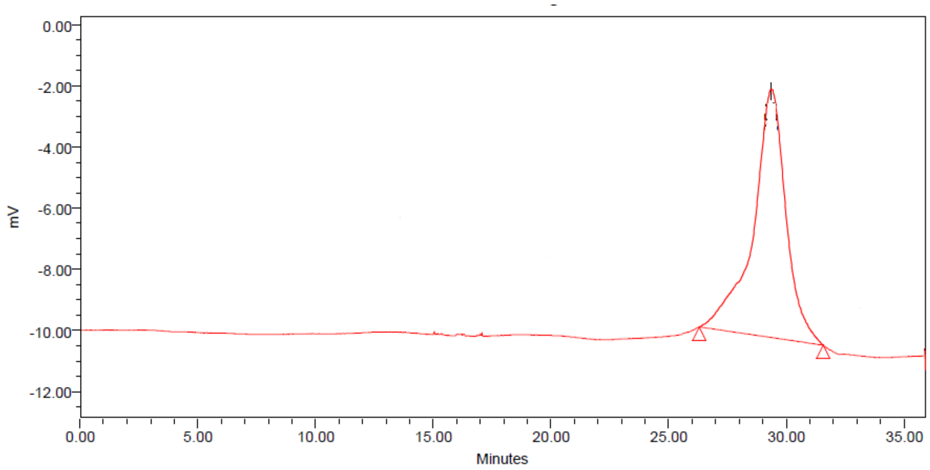


Figure 3.1: GPC trace of BAMO-GLYN copolymer, Mn = 2612 and polydispersity index 1.15.

The FTIR spectrum is shown in Figure3.2. The FTIR spectrum of BAMO-GLYN shows absorption peaksat 3450, 2100, 1640, 1280 and 1150 cm^{-1}, which correspond to hydroxyl groups, azide groups, nitrato groups and polyether linkage,respectively. The absorption at 2850 cm^{-1} was due to methylgroups.

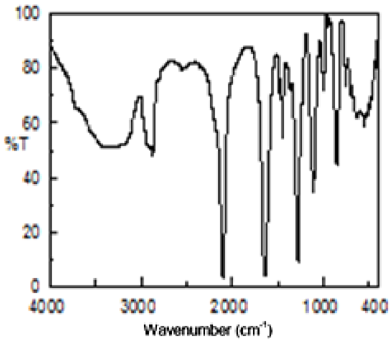


Figure 3.2: FTIR spectrum of BAMO-GLYN copolymer

The ^{1}H-NMR spectrum of BAMO-GLYN is shown in Figure 3.3, while Figure 3.4shows the ^{13}C-NMR spectrum.The ^{1}H-NMR spectrum exhibited signals around 1.3 and 2.2 ppm, which corresponded to the CH_2 protons of the 1,4-butanediol and the hydroxyl group proton, respectively. The peaks between 3.6 and 4 ppm correspond to the $-CH_2N_3$ and $–OCH_2$ protons of the polymer backbone and peaks in the range 4.5 to 5 ppm are of $–CH_2ONO_2$ protons in the branch. The major assignment on ^{13}C NMR spectrum is the signal around 52-55 ppm, which is attributed to the azide attached carbon and the signal around 82-87 ppm, which is attributed to the nitrato group attached carbon. The signal around 69-71ppm is associated with the polyether linkage ($–O–CH_2–$). Solvent peak appears at 77 ppm and the signal around 79 ppm is attributed to the ($–O–CH–$). The strong resonance peaks of methylene protons of 1,4-butanediol in BAMO-GLYN were visible around 25 ppm.

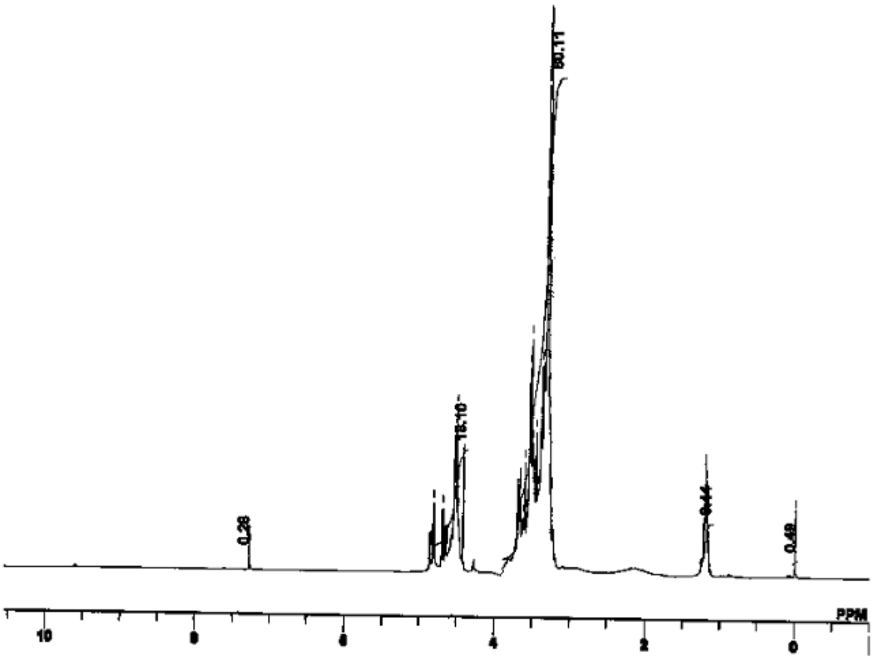


Fig. 3.3: ^{1}H NMR spectrum of BAMO-GLYN copolymer

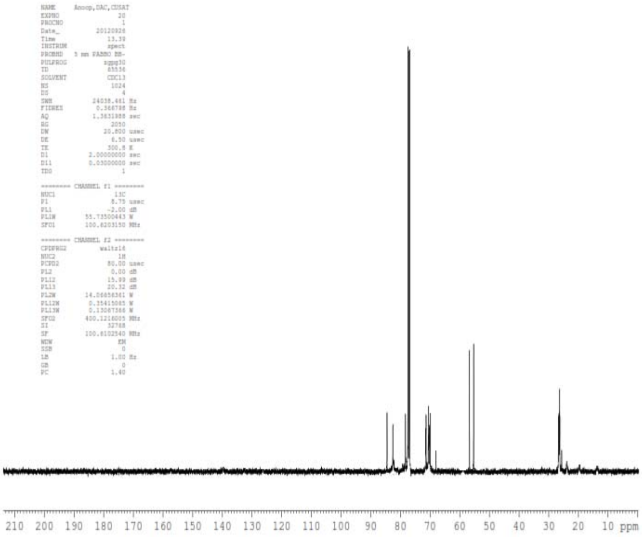


Fig. 3.4: ^{13}C NMR spectrum of BAMO-GLYN copolymer

The BAMO-GLYN copolymer is an yellow, viscous liquid with glass transition temperature (Tg) below room temperature. The thermal analysis of BAMO-GLYN copolymer by using DSC was performed and Figure 3.5 presents the result. The polymer exhibited glass transition temperature of -62 ^{o}C and two exotherms are found at 210 and 240 ^{0}C, which are attributed to the scission of azide and nitrato groups from the polymer backbone.

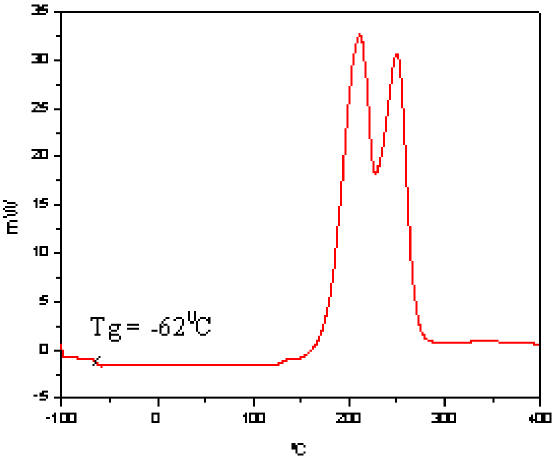


Fig. 3.5: DSC curve of BAMO-GLYN copolymer

The effect of diols on the polymerization reaction was studied by using ethylene glycol (EG) and butanediol (BD) as intiator with different mole ratios. There was not much difference in the polymerization yield. Altering the ratio of reactive monomers to the initiators was also studied and the results obtained are tabulated below. The maximum yield was obtained for the monomer to initiator ratio 1:0.02.

Table 1: Polymerization studies of BAMO-GLYN copolymer

Sl.No	BAMO (in mmol)	GLYN (in mmol)	Type of Diol	Diol (in mmol)	Monomer/ Initiator Ratio	Yield (%)[a]	Mn	PDI
1	1	1	EG	0.1	10	85	2412	1.19
2	4	4	EG	0.1	40	84	2680	1.21
3	1	1	BD	0.02	50	86	2612	1.15
4	4	4	BD	0.02	200	85	2840	1.72

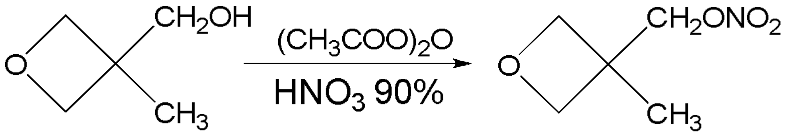
[a]Polymer yield= (weight of the polymer/(weight of BAMO+ weight of GLYN) x 100; [b]Polydispersity Index (PDI) = M_w/M_n

3.2.2 BAMO-NMMO copolymer

BAMO-NMMO copolymer was synthesized from the copolymerization reaction between BAMO and NMMO using BF_3Et_2O as catalyst and 1,4-butanediol as initiator.

3.2.2.1 Synthesis of NMMO

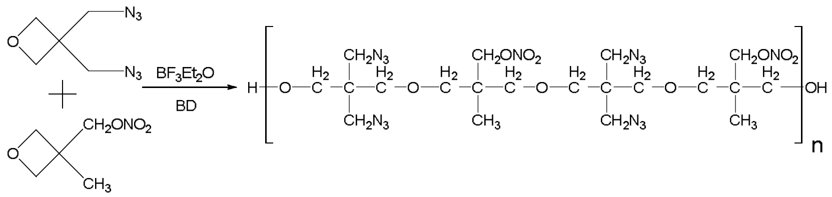
NMMO (3-nitratomethyl-3-methyloxetane) monomer was synthesized from HMMO (Hydroxyl Methyl MethylOxetane) by acetyl nitrate nitration using 90% HNO_3 and acetic anhydride mixture. The yield was found to be 74%.



Scheme 3.5: Synthesis of NMMO

3.2.2.2 Synthesis of BAMO-NMMO copolymer

BAMO-NMMO copolymer was synthesized from the copolymerization reaction between BAMO and NMMO using BF_3Et_2O as catalyst and 1,4-Butanediol as initiator. The polymerization of BAMO was initiated through activated monomer polymerization followed by the addition of NMMO monomer to the reaction mixture in equal mole ratios and the polymerization was terminated by the addition of saturated brine solution.



Scheme 3.6: Synthesis of BAMO-NMMO copolymer

The density of the BAMO-NMMO was found out using a pyknometer, and was found to be1.26 g/ml.

The GPC profile of the BAMO-NMMO is shown in Figure **3.6**. The number average molecular weight was found out using GPC and it was found to be 2880 with polydispersity index 1.21.

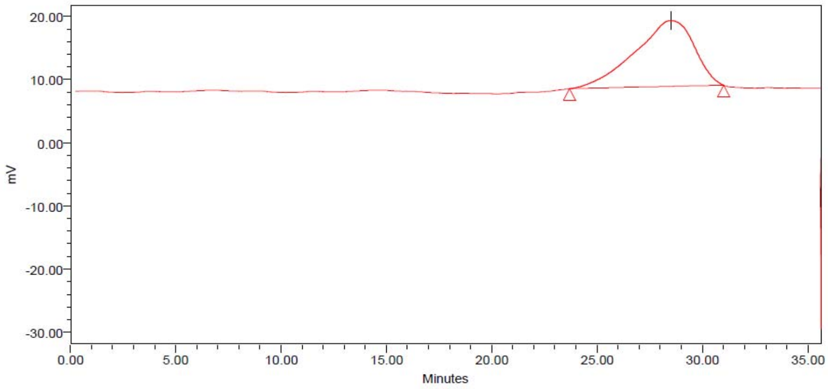


Figure 3.6: GPC trace of BAMO-NMMO copolymer, Mn = 2880 and polydispersity index 1.21.

The FTIR spectrum is shown in Figure 3.7. The FTIR spectrum of BAMO-NMMO copolymer shows major absorption peaksat 2100, 1640, 1280 and 1150 cm^{-1}, which correspond to azide groups, nitrato groups and polyether linkage, respectively. The absorption around 2850 and 3450 cm^{-1} could be attributed to methyland ethyl groups and the hydroxyl groups, respectively.

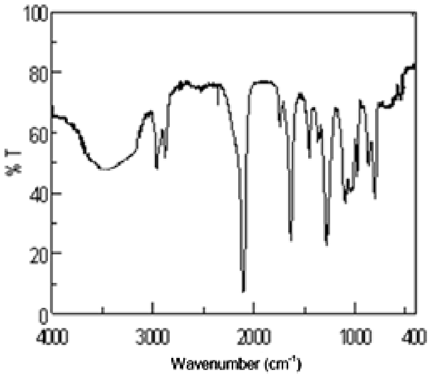


Figure 3.7: FTIR spectrum of BAMO-NMMO copolymer

The ^{1}H-NMR spectrum of BAMO-NMMO is shown in Figure 3.8, while Figure 3.9 shows the ^{13}C-NMR spectrum. The ^{1}H-NMR spectrum exhibited signals at 1.0, 1.3 and 2.2 ppm, which correspond to the CH_3 protons, CH_2 protons of the 1, 4-butanediol included in the polymer and the hydroxyl group proton, respectively. The peaks between 3.6 and 4 ppmcorrespond to the -CH_2 and –OCH- protons of the polymer backbone and peaks in the range 4.5 to 5 ppm are of –CH_2ONO_2 protons in the branch.

Significant peaks in the^{13}C-NMR spectrum of BAMO-NMMO are around 26-28 and at 75ppm. These peaks correspond to the CH_2 of the 1, 4-butanediol. The major assignments on this spectrum are the signal around 52-55 ppm, which is attributed to the azide attached carbon and the signal around 82-87 ppm, which is attributed to the nitrato group attached carbon. The polyether linkage –O–CH_2–signals appear at 69-71 ppm. On the other hand, solvent signal appears at 77ppm and the signalaround 79 ppm is attributed to the –O–CH–. The peak at 17 ppm is due to the methyl group in the branch of the polymer backbone.

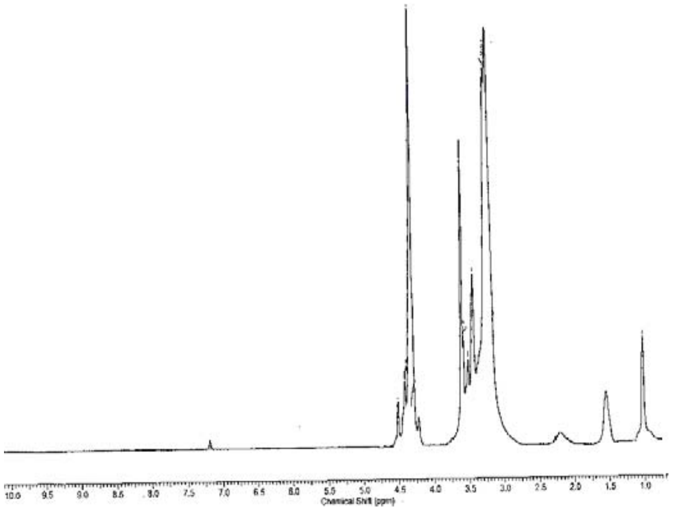


Fig. 3.8: ^{1}H NMR spectrum of BAMO-NMMO copolymer

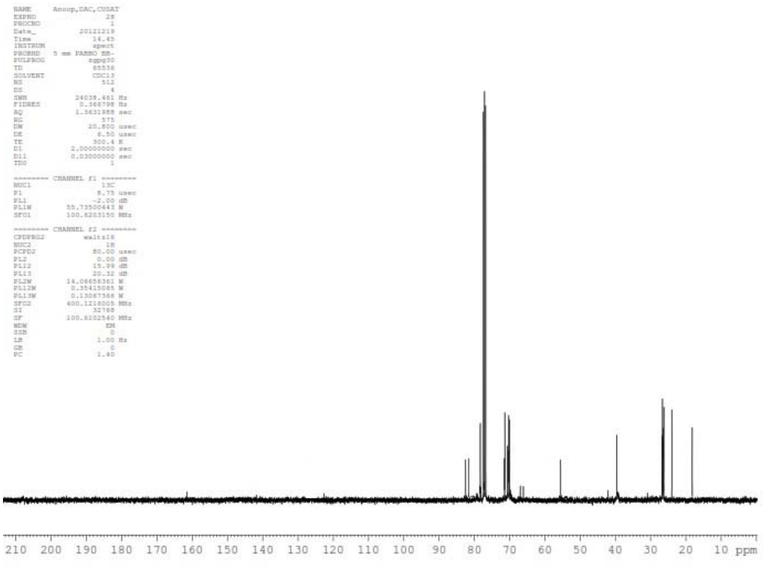


Fig. 3.9: ^{13}C NMR spectrum of BAMO-NMMO copolymer

The decomposition behavior of BAMO-NMMO copolymer was determined from DSC thermogram at hightemperature. Results are presented in Figure 3.10. The DSC scan of BAMO-NMMO shows exothermic peaks in the temperature range 160-240 ^{o}C, with exothermic peak maximum around 250±5 ^{o}C and 200±5 ^{o}C which are due to the scission of nitrato and azide groups in the polymer.

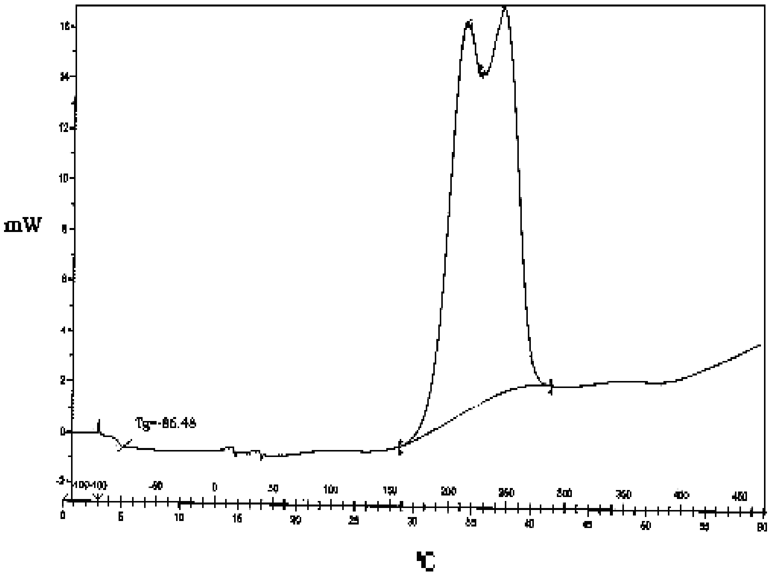


Fig. 3.10: DSC thermogramof BAMO-NMMO copolymer

The effect of diols on the polymerization reaction was studied using ethylene glycol (EG) and butanediol (BD) as intiators with different mole ratios. There was not much difference in the polymerisation yield. Altering the ratio of reactive monomers to the initiators was also studied and the results obtained are tabulated below. The maximum yield was obtained for the monomer to initiator ratio 1:0.02.

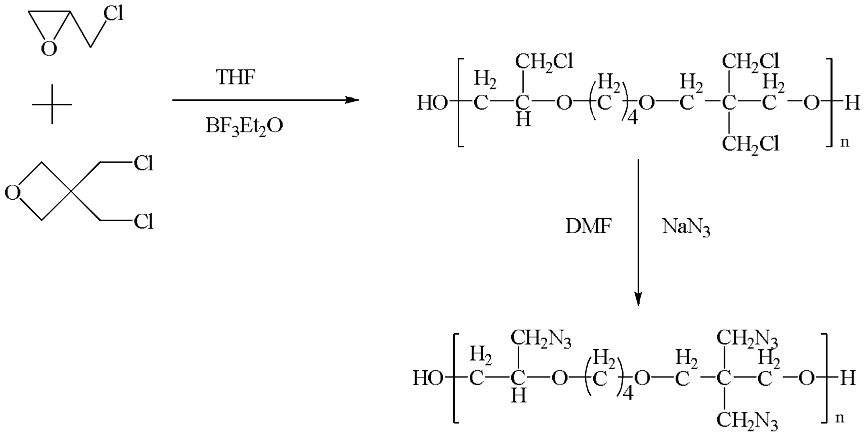
Table 2: Polymerization studies of BAMO-NMMO copolymer

Sl.No	BAMO (in mmol)	NMMO (in mmol)	Type of Diol	Diol (in mmol)	Monomer / Initiator Ratio	Yield (%)[a]	Mn	PDI[b]
1	1	1	EG	0.1	1:0.1	78	2520	1.15
2	3	3	EG	0.1	3:0.1	76	3412	1.37
3	1	1	BD	0.02	1:0.02	82	2880	1.21
4	3	3	BD	0.02	3:.02	81	2840	1.47

[a]Polymer yield = (weight of the polymer/(weight of BAMO+ weight of NMMO) x 100; [b]Polydispersity Index(PDI) = M_w/M_n

3.2.3 GAP-BAMO copolymer

GAP-BAMO copolymer was synthesized by two step process. In the first step, classical cationic polymerization between epichlorohydrin and 3,3-bischloromethyl oxetane was carried out to form a copolymer. In the second step, azidation was carried out with NaN_3 in DMF to form GAP-BAMO copolymer. The copolymerization reaction between ECH and BCMO using BF_3Et_2O and THF is depicted in scheme 3.7.



Scheme 3.7: Synthesis of GAP-BAMO copolymer

The density of the GAP-BAMO copolymer was found out using a pyknometer, and was found to be1.38 g/ml.

The GPC profile of the GAP-BAMO is shown in Figure 3.11. The number average molecular weight was found out using GPC and it was found to be 5224 with polydispersity index 1.42.

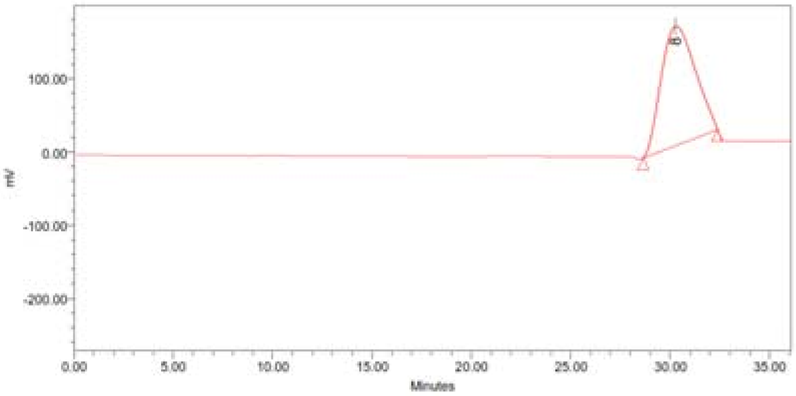


Figure 3.11: GPC trace of GAP-BAMO copolymer, Mn = 5224 and polydispersity index 1.42.

The FTIR spectrum is shown in Figure 3.12. The FTIR spectrum of GAP-BAMO copolymer showsmajor absorption peaksat 2100, and 1150 cm^{-1}, which correspond to azide groups, nitrato groups and polyether linkage, respectively. The absorption around 2850 and 3450 cm^{-1} could be attributed to methyland ethyl groups and the hydroxyl groups, respectively.

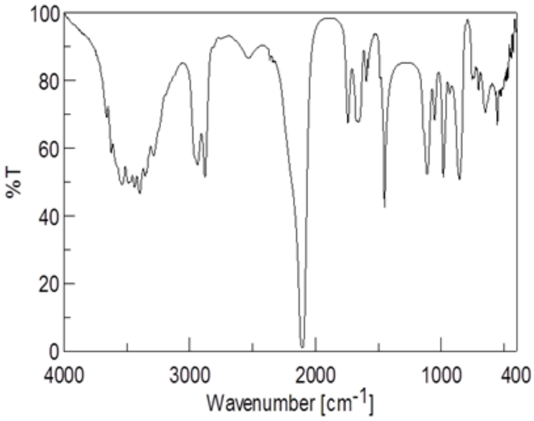


Figure 3.12: FTIR spectrum of GAP-BAMO copolymer

The ^{1}H-NMR spectrum of GAP-BAMO is shown in Figure 3.13, while Figure 3.14 shows the ^{13}C-NMR spectrum. The ^{1}H-NMR spectrum exhibited signals at 1.3 and 2.2 ppm, which correspond to the CH_2 protons of the ring opened THF included in the polymer and the hydroxyl group proton, respectively. The peaks between 3.6 and 4 ppmcorrespond to the -CH_2, - CH_2N_3 and –OCH- protons of the polymer backbone. Major peaks of ^{13}C-NMR spectrum of GAP-BAMO copolymer appears around 26-28 ppm and at 75ppm and these peaks correspond to the CH_2 carbon of the ring opened THF. The major assignments on this spectrum are the signal around 52-55 ppm, which is attributed to the azide attached carbon and the polyether linkage –O–CH_2–peaks appear at 69-71 ppm. On the other hand, solvent absorption appears at 77ppm and a peak around 79 ppm is attributed to the –O–CH–.

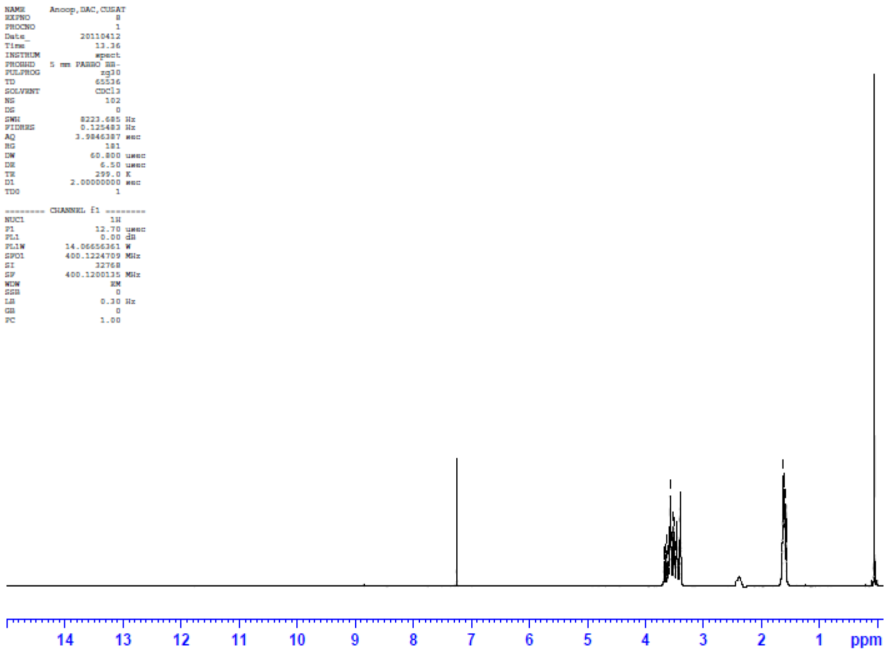


Fig. 3.13: ^{1}H NMR spectrum of GAP-BAMO copolymer

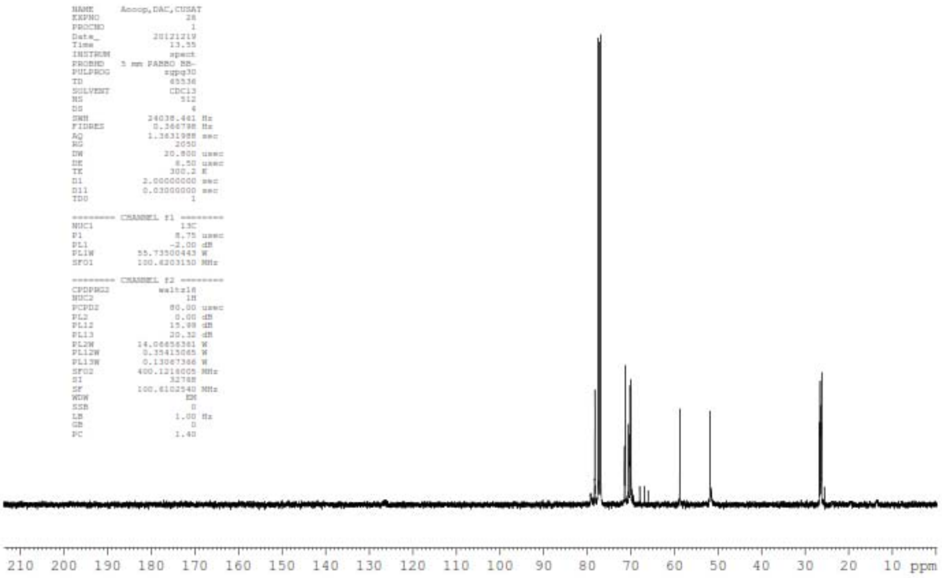


Fig. 3.14: ^{13}C NMR spectrum of GAP-BAMO copolymer

The DSC analysis was carried out at high temperature to study the decomposition behavior of GAP-BAMO copolymer. Results are recorded in Figure 3.15. The DSC scan of GAP-BAMO shows exothermic peaks in the temperature range 160-240 °C, with a maximum peak around 200±5 °C which is indicative of the scission of azide groups.

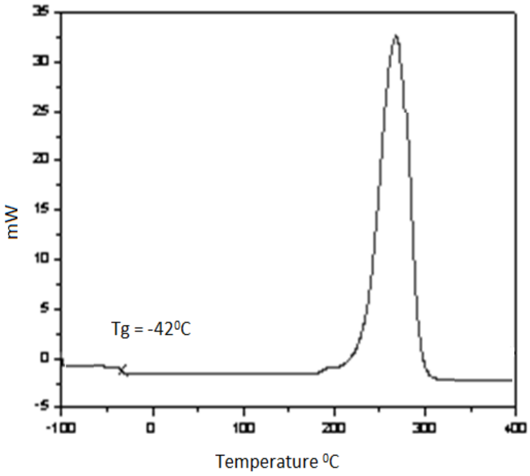


Fig. 3.15: DSC thermogramof GAP-BAMO copolymer

Here also the effect of diols on the polymerization reactions were studied by using ethylene glycol (EG) and butanediol (BD) as intiators with different mole ratios. There was not much diffrence in the polymerisation yield. Altering the ratio of reactive monomers to the initiators was also studied and the results obtained are tabulated in Table 3. The maximum yield was obtained for the monomer to initiator ratio 1:0.02.

Table 3: Polymerization studies GAP-BAMO copolymer

Sl.No.	**BCMO (in mmol)**	**ECH (in mmol)**	**Type of Diol**	**Diol (in mmol)**	**Monomer/ initiator Ratio**	**Yield (%)[a]**	**Mn**	**PDI[b]**
1	1	1	EG	0.1	1:0.1	77	3260	1.25
2	2	2	EG	0.1	2:0.1	72	4420	1.37
3	1	1	BD	0.02	1:0.02	84	5224	1.42
4	2	2	BD	0.02	2:.02	81	4980	1.44

[a]Polymer yield= (weight of the polymer/(weight of ECH+ weight of BCMO) X 100;[b]Polydispersity Index(PDI) = M_w/M_n

3.2.1.4 Hydroxyl value of the polymers

The polymer was treated with standard acetylating agent comprising of acetic anhydride and pyridine. Each sample containing unreacted acids and blanks were titrated with standard NaOH solution. The difference between sample and blank was used to calculate the hydroxyl value of the copolymer.

Table 4: Hydroxyl value of Polymers

Sl. No.	**Polymer**	**Hydroxyl Value (mg KOH/g)**
1	BAMO-GLYN copolymer	58
2	BAMO-NMMO copolymer	52
3	GAP-BAMO copolymer	61

3.3 Conclusion

Thermoplastic elastomers based on both oxetane and oxirane have been synthesized and characterized. The copolymers BAMO-GLYN, BAMO-NMMO and GAP-BAMO could be synthesized successfully. The spectroscopic techniques such as FT-IR, ^{1}H NMR and ^{13}C NMR and DSC are used to characterize the polymers. Hydroxyl values of the synthesized polymers were also evaluated.

3.4 Experimental

3.4.1 Synthesis of BCMO

Pentaerythritol 50 g (0.37 mol) was added to a mixture of DMF and $SOCl_2$, 27 ml (0.23 mol). During the addition, the temperature was maintained at 55 ^{0}C for 1 hour. The solution was slowly heated to 120 ^{0}C for a period of 90 minutes. Thionylchloride 58 ml (0.49mol) was added to the reaction mixture over a period of 3 h while the temperature was maintained at 120 ^{0}C. The reaction mixture was stirred for a period of 6 h and allowed to cool to about 80 ^{0}C. Thereafter, 250 ml of 1.2 M NaOH was added to the cooled reaction mixture, the first 50 ml being added slowly due to the exothermic nature of the reaction. The resulting solution was stirred under reflux condition for 3 h. This mixture was steam distilled in order to separate the 3, 3-bischloromethyloxetane as bottoms. The distillate was extracted with methylenechloride, the extract was combined with the distillation bottoms. The fraction was concentrated and fractionated (80 ^{0}C at 10 mm of Hg) to obtain BCMO. The yield was found to be 56%.

3.4.2 Synthesis of BAMO

Sodiumazide 12.7 g (0.195 mol) was taken in 50% aqueous NaOH solution and BCMO 13.86 g (0.09 mol) was added to it along with a small amount of 0.61 g

(0.0019 mol) phase transfer catalyst, tetraethylammoniumbromide. The biphasic mixture was heated at 95-100 ^{0}C for 24 h. The mixture was cooled, the organic layer was separated and washed with water and passed through a column packed with neutral alumina. The eluent was vacuum dried to yield BAMO of 85%.

3.4.3 Synthesis of GLYN

In a 300 ml, 3 necked R.B flask equipped with a magnetic stirrer, thermometer, dropping funnel and nitrogen purge line, glycerin 70 g (0.76 mol) was added, diluted with methylenechloride (50 ml). The flask was immersed in ice bath and cooled to 5 ^{0}C. 150 ml of HNO_3 (90%) was added drop wise over 30-45 min period and allowed to stir at room temperature for 5-6 h. 30% NaOH solution was added to the nitrated glycerol solution while cooling to maintain the temperature of the mixture to below 25 ^{0}C. When the mixture was observed to have a pH of 14, additional 30% NaOH solution 275 g (6.88 mol) was added slowly to maintain the temperature below 25 ^{0}C.The mixture was allowed to stand for about 0.5 h, and extracted 3 times with ether. The organic phase was combined, dried with $MgSO_4$, filtered and evaporated under vacuum, providing approximately 44 g of pure glycidylnitrate. The yield was found to be 70%.

3.4.4 Synthesis of BAMO-GLYN copolymer

In a double necked R.B flask fitted with a condenser and a magnetic stirrer, 5 ml of methylenechloride was taken. 1,4-butanediol 0.11 ml (1.2 mmol) and BF_3 etherate 0.30 ml (2.4 mmol) in the ratio (1:2) was added. This was allowed to react for 1h. BAMO 10 g (60 mmol) dissolved in 100 ml methylenechloride was added and kept to react for 1 h. GLYN 7 g (60 mmol) was added dissolved in 100 ml methylenechloride slowly. The mixture was stirred at room temperature for 36 h. 50 ml NaCl solution was added to terminate the polymerization. The organic layer was separated and washed with 100ml saturated $NaHCO_3$ solution. The organic layer was dried over $MgSO_4$ and filtered off the $MgSO_4$. The resulting solution was added to excess of cold ethanol. The solvent was removed under reduced pressure to yield 85% of a highly viscous liquid.

3.4.5 Synthesis of NMMO

In a 100 ml, 3 necked R.B flask equipped with a magnetic stirrer, thermometer and a dropping funnel, along with acetyl nitrate solution was added which was prepared by stirring, 1.4 ml of 90% HNO_3 to 6.2 ml (0.06 mol) of acetic anhydride at 20 ^{0}C.The solution was cooled to 5 ^{0}C. To this mixture a solution of 3 g (0.029 mol) of HMMO diluted with 8 ml of $CHCl_3$ was added drop wise. The temperature was maintained at -10 ^{0}C during the addition and for a further 15-30 min. The reaction was quenched by pouring over 6.2 g of $NaHCO_3$ followed by the addition of water and very rapid stirring. After the mixture was determined to have a pH 7 or 8, the organic layer was washed with distilled water and dried over $MgSO_4$. The required product was obtained in polymerizable purity by passing it through a basic alumina column and eluting with 50/50 vol/vol $CHCl_3$/hexane.Yield of NMMO was found to be 90%.

3.4.6 Synthesis of BAMO-NMMO copolymer

In a double necked R.B flask fitted with a condenser and a magnetic stirrer, 5 ml dichloromethane was taken.1,4-butanediol and BF_3etherate in the ratio (1:4) (0.01ml (0.1 mmol) 1,4-butanediol and 0.76 ml (0.4 mmol) BF_3etherate) were taken. This was allowed to react for 1h. 0.5 g (2.98 mmol) of BAMO and 0.44 g (2.98 mmol) of NMMO was dissolved in 10 ml methylenechloride was added at one time. The mixture was stirred at room temperature for 48 h. 0.2 ml saturated NaCl solution was added to terminate the polymerization. The phases were separated and the aqueous phase was extracted with 5 ml of CH_2Cl_2. The combined organics were dried over $MgSO_4$ and filtered off the $MgSO_4$. The solvent was removed under reduced pressure to afford 92% of a pale yellow oil product.

3.4.7 Synthesis of GAP-BAMO copolymer

In a double necked R.B flask fitted with condenser and a magnetic stirrer, 100 ml dichloromethane was taken with 0.82 ml of THF (10 mmol). To this mixture, drops of 0.5 ml (4 mmol) BF_3etherate were added, using a dropping funnel and the mixture was cooled to 0 to 5 ^{0}C for 1 h and 0.78 ml (10 mmol) of ECH dissolved in 10 ml of polymerization solvent was added drop wise over a period of 1h using a dropping funnel. After one hour 1.7 g (10 mmol) of BCMO in DCM was added drop wise to the reaction mixture over a period of two hours. The resulting mixture was stirred at ambient temperature for 72 h. The polymerization was terminated by adding distilled water and vigorously stirring for about 30 min. The crude reaction product was transferred to a separating funnel and the organic layer was washed three times with distilled water in order to remove all unreacted monomer, diol, and catalyst. The organic layer was transferred to a round-bottom flask and dried over magnesium sulfate.

PECH-BCMO 2 g (12.2 mmol) was dissolved in dimethylformamide (5 mL) and introduced into the flask. The reaction mixture was heated slowly until the polymer was dissolved in the solvent (maximum temperature 60 ^{o}C). About 0.378 g of NaN_3 (37 mmol) was transferred in small portions within ½ an hour and TBAB 0.039 g (0.1 mmol) was also added to the reaction mixture.The mixture was heated for 48 h at 120 ^{0}C. The polymer solution was diluted to twice the volume of DMF with dichloromethane. The mixture was filtered to separate the unreacted sodium azide and the formed sodium chloride. The DCM solution was removed under vacuum and the resulting viscous liquid was transferred to a separating funnel and washed several times with hot water to remove traces of DMF. Two layers appeared in the separating funnel and DCM was added to extract the polymer. A solution of polymer in dichloromethane was dried over magnesium sulfate and the pure polymer was obtained by removing the solvent by rotary vacuum evaporator. The polymer formed was an amper colored viscous liquid with yield 90%.

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Chapter 4

SYNTHESIS AND CHARACTERIZATION OF POLYPHOSPHAZENE BASED ENERGETIC POLYMERS

Abstract

Polyphosphazene based energetic polymers can act as new class of binders for both rocket propellants and insensitive munitions, which practicallybeat conventional carbon-based systems in terms of their energy-densities and glass transition temperatures. Polyphosphazenes are well known for their mechanical properties especially linear polyphosphazenes are found to exhibit low Tg and molecular weight. Energetic groups in linear polyolyphosphazene make them energetic polyphosphazenewhich will bind the explosive formulations. Energetic polymers based on polyphosphazene such as poly(bistrifluoroethoxy) phosphazene (PTEP), poly(dinitropropanoxy) phosphazene (PDNPP), Poly [bis(4-nitrobenzenamine)] phosphazene (PNBP) and Poly[bis(3,5-dinitrobenzenamine)] phosphazene (PDNBP) would replace the conventional binder systems. PTEP was synthesized by the nucleophilic substitution of sodiumtrifluoroethanolate on the polydichlorophosphazene (PDCP) back bone. PDNPP was prepared in two steps, first step was the substitution of sodium salt of glycidol in the PDCP and second step was the nitration of the resulting polymer with 90% HNO_3. The polymer PNBP and PDNBP was synthesized by the reaction of PDCP with 4-nitroaniline and 3,5-dinitroaniline using triethylamine in THF. The synthesized polymers were characterized by GPC for molecular weight determination, FTIR and NMR spectroscopy for structural confirmation. Thermal analysis using DSC showed a glass transition temperature around -63 ^{0}C and exothermic decomposition around 350 ^{o}C for PTEP, a glass transition temperature around -60 ^{0}C and exothermic decomposition around 220 ^{o}C for PDNPP. But the polymers PNBP and PDNBP, exhibited a glass transition temperature at -20 ^{0}C and -5 ^{0}C with an exothermic decomposition at 230 ^{o}C was observed.

Keywords:* *Energetic *Polyphosphazene, PDCP, Energetic Binder.*

4.1 Introduction

There is no weapon system or type of weaponry that doesn’t rely on energetic materials-either in the form of an explosive fill or as a propellant. In addition, energetic materials are used in a multitude of critical defense components ranging from shaped charges, actuators and delay lines to detonators. The need for increased mobility, enhanced range and lethality, reduced or modified signatures, reduced collateral damage, and the capability to destroy hardened and buried targets combine to increased demand for enhanced conventional energetics. Crystalline high energy density materials such as RDX (1,3,5-trinitro-1,3,5-triazacyclohexane) and HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane) possess very high melting point which renders them difficult to shape for use in explosive charges. They are sensitive to shock and mechanical stimuli due to their crystallinity coupled with high energy density, thus diminishing their handling utility and general safety in manufacturing and service environments.

Present day’s energetic binders like polyBAMO (poly (Bisazidomethyl oxetane), polyNMMO[poly(nitratomethyl methyl) oxetane], polyGLYN [poly(glycidyl nitrate)] etc. are more widely used. The energetic polymer binders such as polyBAMO, polyNMMO, polyGLYN etc may be used in conjugation with high explosives such that the energy of the explosive itself is not overlay diminished by the presence of binder in the combined material. The difficulty with this approach is in obtaining energetic polymers, which when used as binders have an adequate combination of both desirable physical properties such as malleability and shock insensitivity, in addition to high energy density. Even the best energetic binders have energy densities that are significantly lower than that of the crystalline explosive material for which they are required to bind. This has the effect of reducing the energetic performance of the explosives. In an attempt to solve this problem, current practice is to use a high loading of explosive relative to binder which in turn diminishes the desirable physical properties of the binder/explosive mixture. Energetic polyphosphazenes [1-5] containing energetic functional groups such as azide ($-N_3$), nitrato ($-ONO_2$), can function as novel binding material for EM formulations.

The energetic polyphosphazene [6-14] as thermoplastic elastomeric binder is an emerging field of research. The energetic polyphosphazenes have potential use over conventional systems and indeed not just as explosive binders, but also for use in propellant and pyrotechnic formulations. The materials possess high energy density and are highly amenable to chemical modification thereby allowing for modification of the physical properties of the material [15-21]. In particular the tacky and rubbery nature of these materials makes them ideal for shaping co-binder materials.

4.2 Results and Discussion

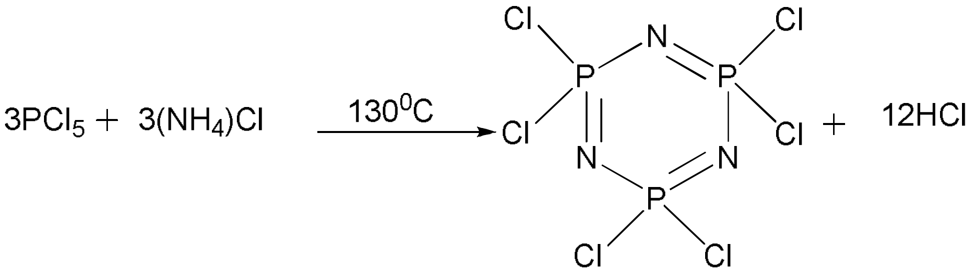
This section deals with the results obtained from the synthesis andcharacterization of hexachlorocyclotriphosphazene (HCCTP) monomer, polydichlorophosphazene (PDCP) polymer precursor, poly (bistrifluoroethoxy) phosphazene (PTEP), poly(dinitropropanoxy) phosphazene (PDNPP), poly [bis(4-nitrobenzenamine)] phosphazene (PNBP) and poly[bis(3,5-dinitrobenzenamine)] phosphazene (PDNBP).

4.2.1 Synthesis and characterization of poly(dichlorophosphazene) (PDCP)

Section 4.2.1 includes results of the synthesis of hexachlorocyclrotriphosphazene, the monomer, and its polymerization for the synthesis of PDCP and the solvent free synthesis of PDCP.

4.2.1.1 Synthesis of Hexachlorocyclotriphosphazene (HCCTP)

Hxachlorocyclotriphosphazene (HCCTP) was synthesized by reacting phosphorous pentachloride (PCl_5) and ammonium chloride (NH_4Cl) in chlorobenzene solvent at elevated temperature in the presence of ZnO and quinoline catalyst. It was obtained as colorless crystal with melting point 115 ^{0}C and the yield was found to be 80%.



Scheme 4.1: Synthesis of HCCTP

The FTIR spectrum of the HCCTP is shown in Figure 4.1. The important characteristic peaks are the absorption peaks at 1312 and 1216cm^{-1}, which correspond to the phosphorous nitrogen bond (-P=N-). Absorptionpeak around 874 cm^{-1}is attributed to the -P-N- stretching vibrations. In the IR spectrum, the peak around1194 cm^{-1} is due to the-P-N-hexatomic ring frame vibration. The peaks at 523 and 600 cm^{-1} are due to the P-Cl vibration. From comparison with the infrared spectrum of HCCTP from literature, it is observed that all the characteristic peaks are found in the IR spectrum of the product which ensures that the product of the synthetic reaction is hexachlorocyclotriphosphazene.

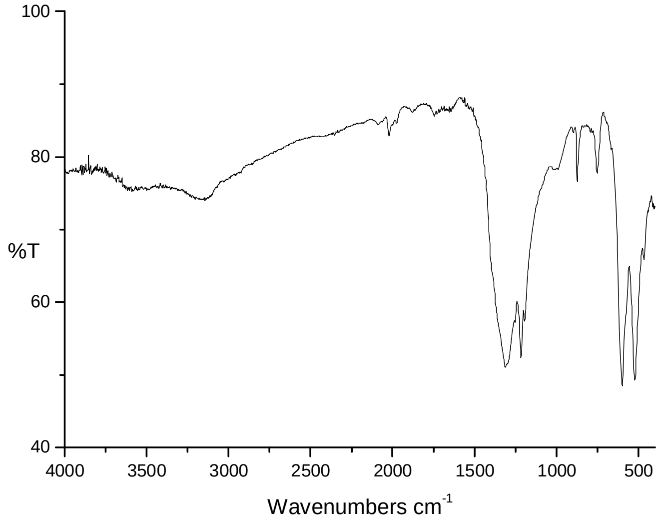
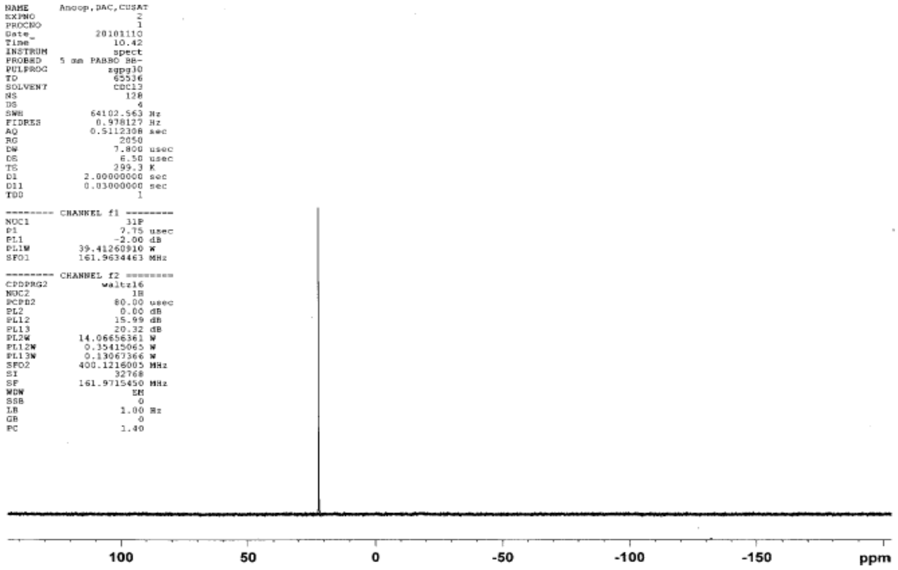


Figure 4.1: FTIR spectrum of HCCTP

HCCTP was characterized by ^{31}P-NMR spectrum, as shown in Figure 4.2. The important feature of this spectrum is the singlet around 21 ppm, which is assigned to three equivalents of phosphorous in the ring and it is confirmed from the literature.



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NAME       Anoop,DAC,CUSAT
EXPNO                    2
PROCNO                   1
Date_             20101110
Time                 10.42
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    128
DS                      4
SWH             64102.563 Hz
FIDRES           0.978127 Hz
AQ              0.5112308 sec
RG                   2050
DW                  7.800 usec
DE                   6.50 usec
TE                  299.3 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  31P
P1                   7.75 usec
PL1                 -2.00 dB
PL1W          39.41260910 W
SFO1          161.9634463 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  0.00 dB
PL12                15.99 dB
PL13                20.32 dB
PL2W          14.06656361 W
PL12W          0.35415065 W
PL13W          0.13067366 W
SFO2          400.1216005 MHz
SI                  32768
SF            161.9715450 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

Figure 4.2: ^{31}P NMR spectrum of HCCTP

The effect of ratio of NH_4Cl and PCl_5 in the reaction yield was studied and found that the reaction yield wasmaximum for the ratio 1.3:1. Above this ratio it was found that the reaction yield was lowered. The results of these studies are tabulated below (Table 4.1).

Table 4.1: Effect of reactant mole ratio on the reaction

Sl.No	PCl_5 to NH_4Cl mol ratio	Solvent	Yield (%)
1	0.9:1	C_6H_5Cl	35
2	1:1	C_6H_5Cl	46
3	1.2:1	C_6H_5Cl	64
4	1.3:1	C_6H_5Cl	72
5	1.4:1	C_6H_5Cl	62
6	1.5:1	C_6H_5Cl	55

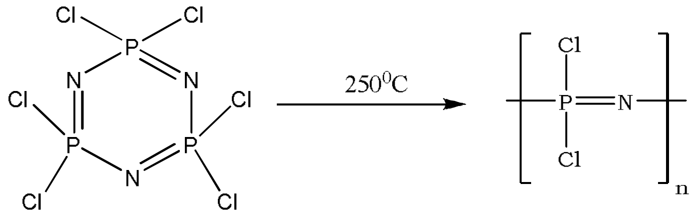
The effect of reaction time on the yield of the reaction was also studied. It was found that, after the addition of catalyst and PCl_5 the reaction gave maximum yield, if it was continued for 3.5 to 4.0 hours.

Table 4.2: Effect of reaction time on the reaction

Sl.No	Reaction Time (in h)	Solvent	Yield
1	3	C_6H_5Cl	66
2	3.5	C_6H_5Cl	72
3	4	C_6H_5Cl	68
4	4.5	C_6H_5Cl	62
5	5	C_6H_5Cl	52
6	5.5	C_6H_5Cl	44

4.2.1.2 Synthesis of poly(dichlorophosphazene) (PDCP)

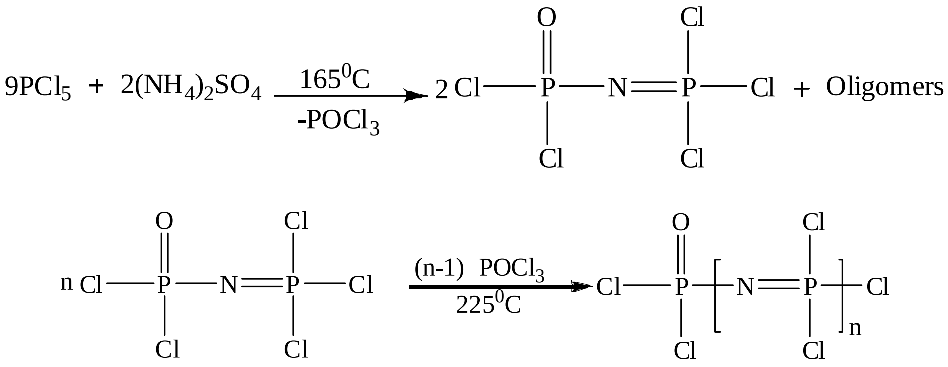
PDCP was prepared from HCCTP by high temperature ring opening in inert atmosphere at 225 ^{0}C for 1 h and then at 250 ^{0}C for 16 h. The polymer was isolated as a colourless rubbery material upon precipitation into an excess of anhydrous hexane from THF.The number average molecular weight of the polymer was found to be 4250 with polydispersityindex 1.2.



Scheme 4.2 Synthesis of PDCP

4.2.1.3 Solid state synthesis of poly(dichlorophosphazene) (PDCP)

PDCP was synthesized by reacting $(NH_4)_2SO_4$ and PCl_5 at 165 ^{0}C and distilling off the $POCl_3$ over a temperature of 225 ^{0}C to yield a viscous colourless rubbery material. The polymer yielded linear low molecular weight with yield 70%. The number average molecular weight was found to be 2420 with polydispersityindex 1.1 (Figure. 4.3).



Scheme 4.3 Synthesis of PDCP

The advantage of this method is that PDCP can be synthesized in a short period of time and it produces low molecular weight linear polymers.

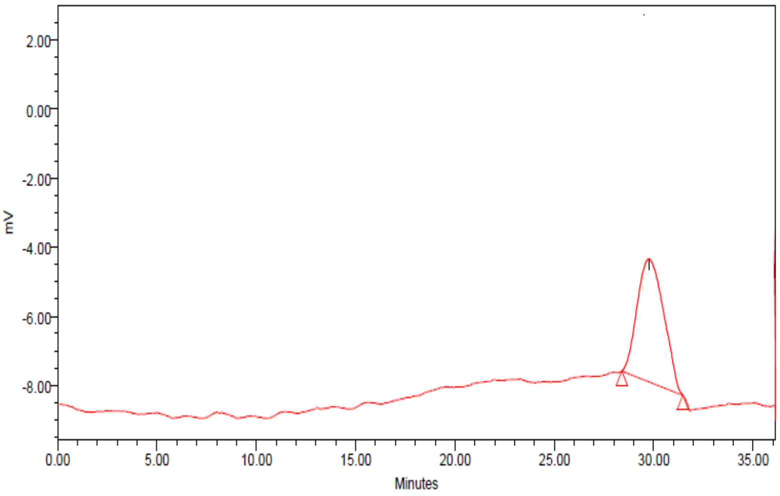


Figure. 4.3: GPC trace of PDCP, Mn = 2420 and polydispersity 1.1.

The FTIR spectrum of the PDCP is shown in Figure 4.4. The important characteristic peaks are the absorption peaks around1312 and 1216 cm^{-1}, which correspond to the phosphorous nitrogen bond (-P=N-). Absorption peak around 774 cm^{-1} is attributed to the -P-N- stretching vibration. The peaks at 584 and 524 cm^{-1} are due to the P-Cl vibration.

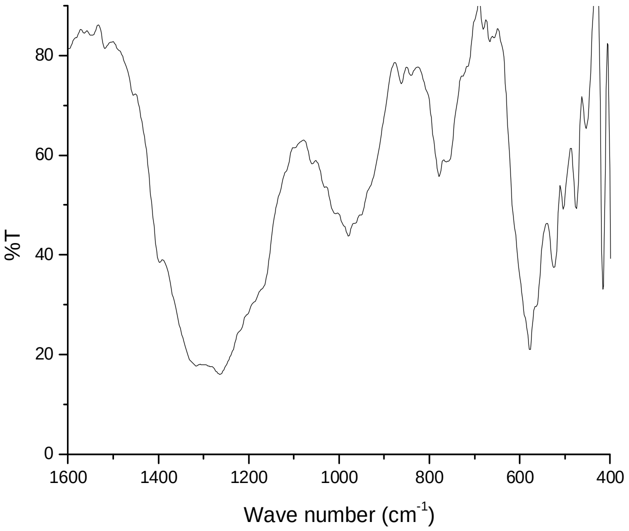
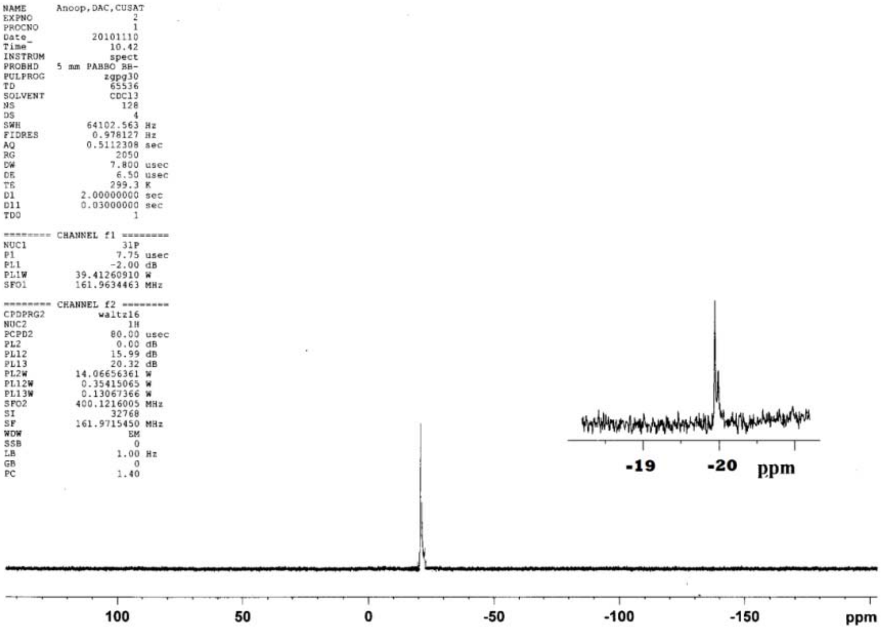


Figure 4.4: FTIR spectrum of PDCP

The formation of the polymer was confirmed by analysing the ^{31}P NMR spectrum in $CDCl_3$(Figure 4.5). The NMR spectrum gives a signal at -20ppm which is the characteristic peak of the PDCP and it showed a low glass transition temperature of -84 ^{0}C (Figure 4.6).



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P1                   7.75 usec
PL1                 -2.00 dB
PL1W          39.41260910 W
SFO1          161.9634463 MHz

======== CHANNEL f2 ========
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PL12                15.99 dB
PL13                20.32 dB
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Figure 4.5: ^{31}P NMR spectrum of PDCP

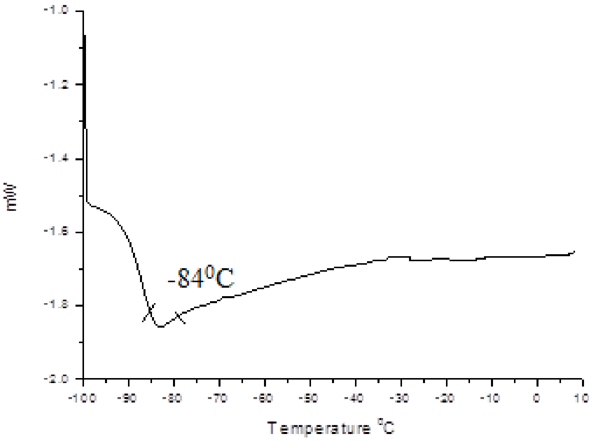
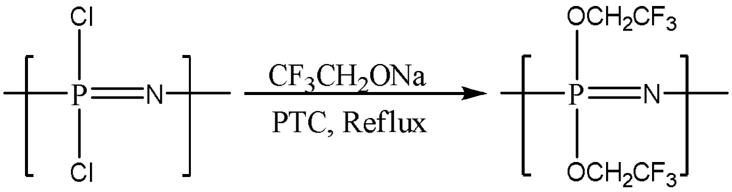


Figure 4.6: DSC curve of PDCP

4.2.2 Synthesis of poly(bistrifluoroethoxy)phosphazene (PTEP)

PTEP was prepared in the same way as that of poly(bistrifluoroethoxy) oxirane (PBTEO)was synthesized and the only difference is in the mole ratio of the reactants taken and the reaction time. Sodium salt of trifluoroethanol on reaction with PDCP in THF under inert atmosphere yielded PTEP as tacky off-white polymer with molecular weight 4872 and polydispersityindex 1.21(Figure.4.7).



Scheme 4.4: Synthesis of PTEP

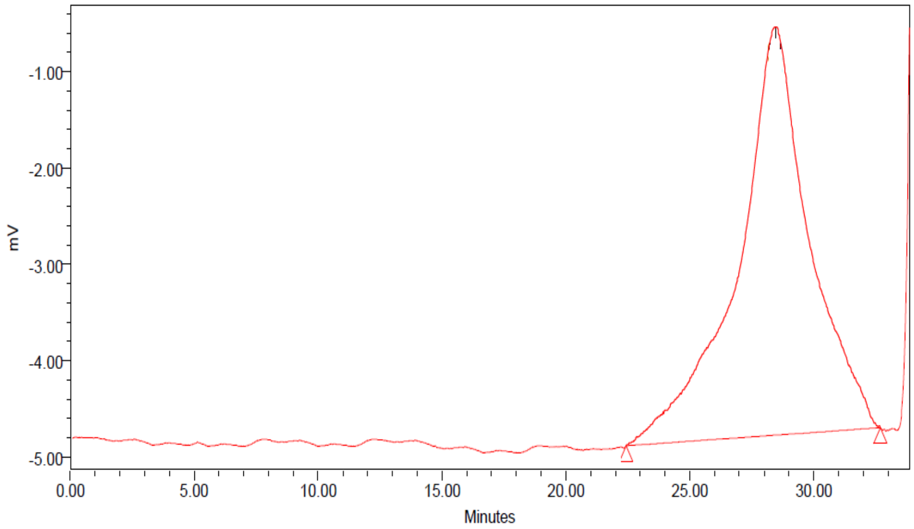


Figure 4.7: GPC trace of PDCP, Mn = 4872 and polydispersity 1.21.

The polymer PTEP was characterized by FT-IR Spectroscopy. FT-IR spectrum of the PTEP is shown in Figure 4.8. The importantcharacteristic peaks are the absorption peaks around 1314 and 1216 cm^{-1}, which correspond to the phosphorous nitrogen bond (-P=N-). Absorption peak around 874 cm^{-1} is attributed to the -P-N- stretching vibration. In the IR spectrum, the peaks at 523 and 600 cm^{-1} due to the P-Cl absorption are absent which indicates that the substitution was successfully carried out. The peaks around 1100 and 1350 cm^{-1}, correspond to the polyether linkage and CF_3groups, respectively. Absorption peaks around 2850 cm^{-1} is attributed to the methylene group.

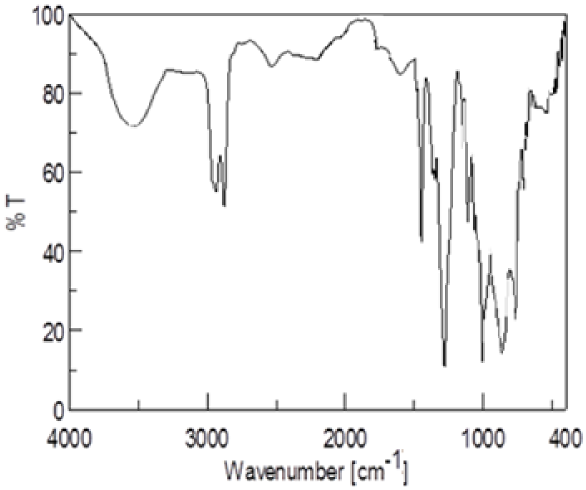


Figure 4.8: FTIR spectrum of PTEP

The formation of the polymer was confirmed by analysing the ^{31}P and ^{1}H NMR spectra in acetone d_6. The ^{31}P NMR gives a broad signal at -7.5 ppm which is the characteristic peak of the PTEP and the ^{1}H NMR spectrum showed a broad signal at 4.5 ppm attributed to $–CH_2CF_3$ and the signal at 2.0 ppm is the solvent peak. The ^{13}C-NMR spectrum of PTEP showed a signal around 61-63 ppm, which is attributed tothe $-CH_2$ of the $–CH_2CF_3$ groups. The signal around 124 ppm which appears as a quartet is attributed to the $–CF_3$ carbon atom of the $–CH_2CF_3$.

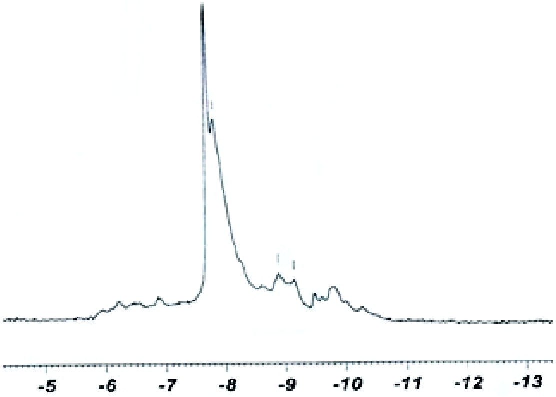


Figure 4.9: ^{31}P NMR spectrum of PTEP

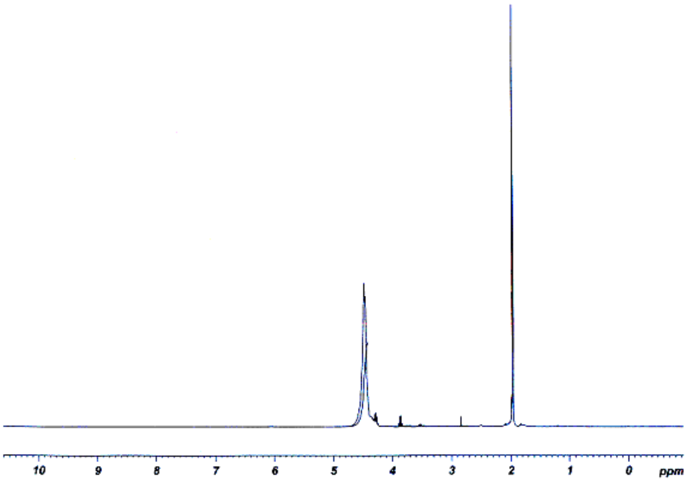


Figure 4.10: ^{1}H NMR spectrum of PTEP

PTEP is an off-white tacky material and its thermal behavior at low temperature representsan important feature for polymeric materials used in propellant formulation and it can be used as precursor for the generation of novel energetic polyphosphazenes. The thermal analysis of PTEP was performed by DSC and Figure 4.11 shows the results for a low temperature scan. The PTEP showed glass transition temperature around -63 ^{o}C, which is suitable for a binder. The decomposition temperature of the PTEP was determined from a DSC thermogram at high temperature. Results are recorded in Figure 4.12. The DSC scan of PTEP shows an exothermic peak in the temperature range 310-360 °C, with a maximum around 350±5 °C and it was due to the scission of the CF_3 bonds from the $–CH_2CF_3$ groups of the PTEPpolymer.

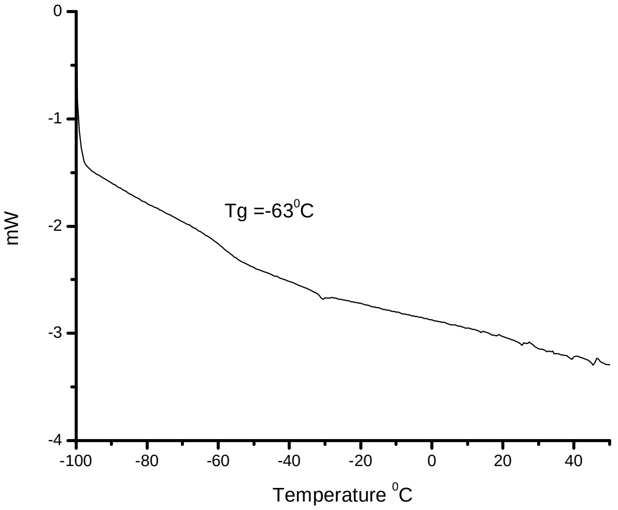


Figure 4.11: The DSC curve of PTEP

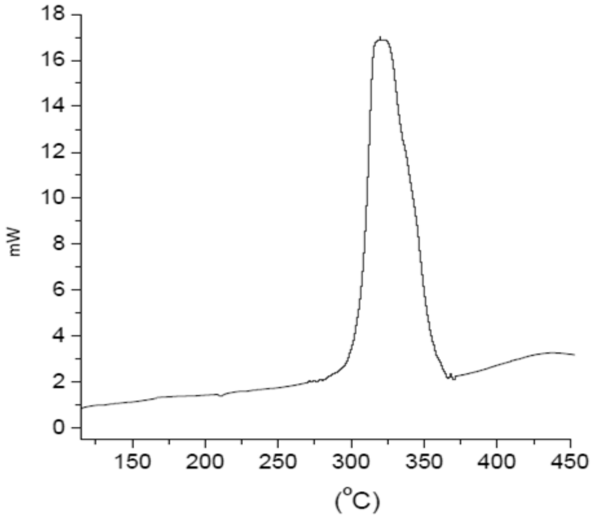


Figure 4.12: DSC thermogram of PTEP

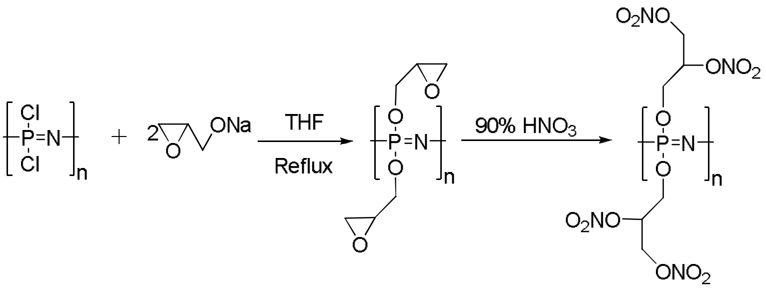
The effect of catalyst and solvent on the conversion of PDCP to PTEP was investigated by varying the amount of catalyst and solvent used. It was found that, THF was the solvent of choice and it gave maximum yield in a short period of time compared to diglyme. The amount of phase transfer catalyst plays a crucial role in the reaction. The amount of catalyst for the current reaction was optimized. The table 4.3 describes the effect of catalyst and the solvent on the conversion of PDCP to PTEP.

Table 4.3: Effect of catalyst and solvent on the reaction

Sl.No.	Polymer PDCP (mmol)	Sodium trifluoroethanolate (mmol)	Catalyst (TBAB) (mmol)	Solvent (THF/Diglyme)	Polymer yield (%)	Reaction Time (h)
1	8.62	17.24	1.72	THF	75	60
2	8.62	17.24	0.86	THF	67	60
3	8.62	17.24	0.86	Diglyme	54	72
4	8.62	17.24	1.72	Diglyme	58	72

4.2.3 Synthesis of poly(dinitropropanoxy) phosphazene (PDNPP)

Synthesis of the polymer PDNPP was done in two steps. The first step was substitution of sodium salt of glycidol in the polymer PDCP and nitration of the same using 90% HNO_3. In this study, substitution of PDCP followed by nitration yielded a polymer with a polydispersity 1.4.



Scheme 4.5: Synthesis of PDNPP

The density of PDNPO was determined by using a pyknometer, and was found to be1.25 g/ml.

The GPC profile of the PDNPO is shown in Figure 4.13. In the nitration reaction, the glycidol ring was opened and got nitrated, which led to an increase in the molecular weight.The number average molecular weight was found out using GPC and it was found to be 5342 with polydispersity index 1.4.

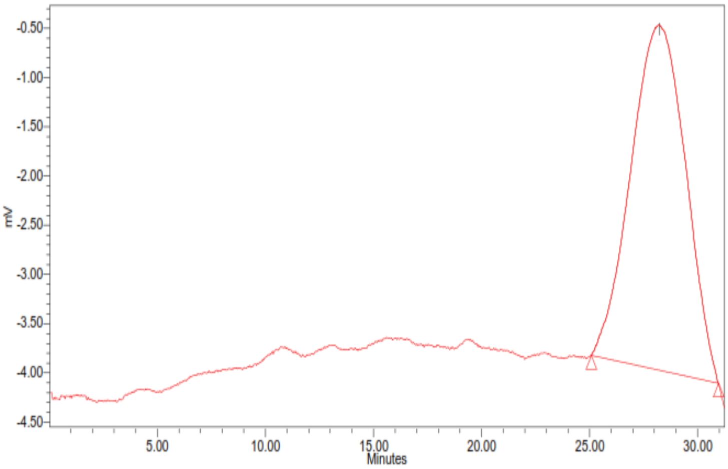


Figure 4.13: GPC trace of PDNPP Mn= 5342 with polydispersity 1.4.

The FTIR spectrum of the PDNPP is shown in Figure 4.14. The absorption peaks around 1640 and 1264 cm^{-1}, correspond to asymmetric and symmetric stretching vibrations, respectively of the nitrato groups. Absorption peaks around 2852 cm^{-1} is attributed to the methylene group. In the IR spectrum, the disappearance of the peak around 745 cm^{-1} and the formation of the peaks at 1634cm^{-1} and 1264 cm $^{-1}$ are attributed to thereplacement of chloro groups of PDCP with the nitrato groups. The other importantpeaks are the absorption peaks around 1314 and 1216 cm^{-1}, which correspond to the phosphorous nitrogen bond (-P=N-). Absorption peak around 874 cm^{-1} is attributed to the -P-N- stretching vibration. In the IR spectrum, the peaks at 523 and 600 cm^{-1} due to the P-Cl absorption are absent which indicates that the substitution was successfully carried out.

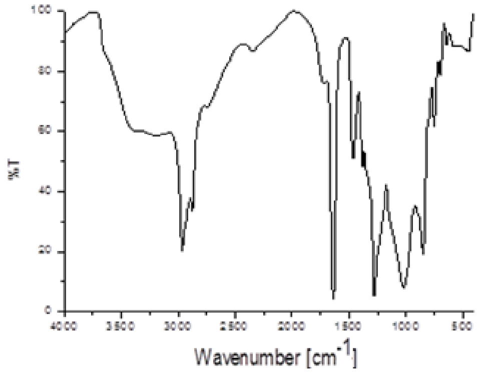


Figure 4.14: FTIR spectrum of PDNPP

The formation of the polymer was confirmed by analysing the ^{31}P, ^{1}H and ^{13}C NMR spectra recorded in $CDCl_3$. The ^{31}P NMR spectrum gives a broad signal at -6.5 ppm which is the characteristic peak of the PDNPP. The important features of the ^{1}H NMR spectrum are the signal around 5.2 ppm, as multiplet which corresponds to the $-CH_2ONO_2$ protons and 3.8 ppm of $–OCH_2$ and 3.5 ppm of –CH respectively. The ^{13}C-NMR spectrum of PDNPP, gives the signal around 92-95 ppm, which is attributed tothe nitrato groups attached carbon. The signal around 69-71 ppm is associated with thepolyether linkage ($–O–CH_2–$) and solvent peak appears at 77 ppm.

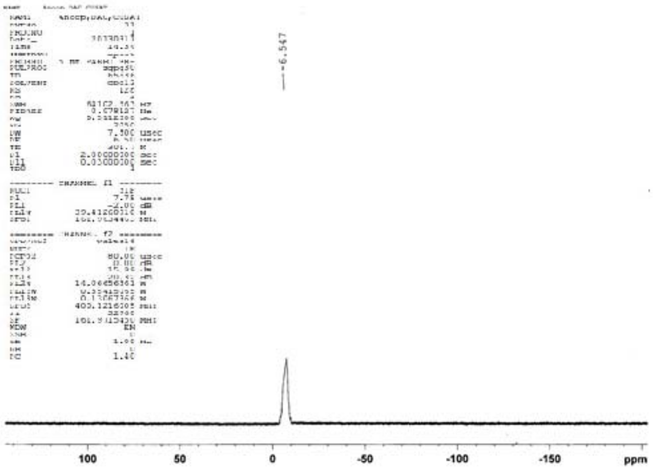


Figure 4.15: ^{31}P NMR spectrum of PDNPP

Poly (dinitropropan-1-oxy)phosphazene (PDNPP) is an yellow highly viscous liquid. The thermal analysis of PDNPP was performed by DSC and Figure 4.16 shows the results for a low temperature scan. The PDNPP showed glass transition temperature around -60 °C, which is suitable for a binder. The decomposition temperature of the PDNPP was determined from a DSC thermogram at high temperature. The DSC scan of PDNPP shows an exothermic peak in the temperature range 190-240 °C, with a maximum at 220±5 °C and it was due to the elimination of $–ONO_2$ by the scission of the CH_2ONO_2 groups from the PDNPP polymer.

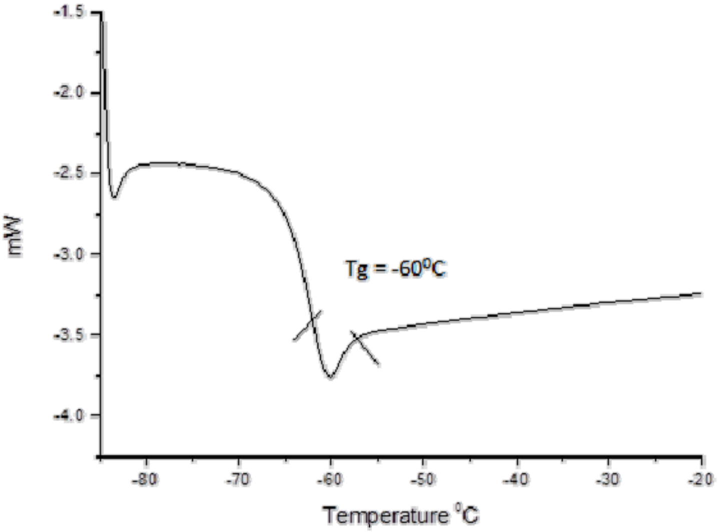


Figure 4.16: DSC curve of PDNPP

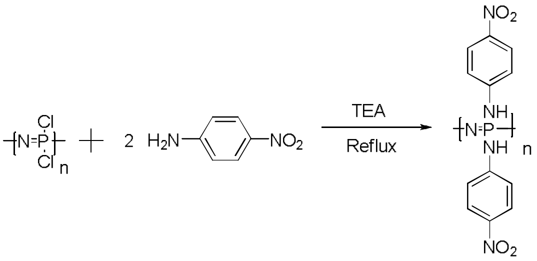
The effect of phase transfer catalyst and solvents in the synthesis of PDNPP was investigated. The yield of the polymer obtained was maximum when THF was used as the solvent. Fully substituted polymer was obtained in the case when the sodium salt of glycidol used was more than 1.5 times that of PDCP. The results of the studies are given in the table 4.4.

Table 4.4: Effect of catalyst and solvent in the synthesis of PDNPP

Sl.No.	Polymer PDCP) (mmol)	Sodium salt of Glycidol (mmol)	Catalyst (TBAB) (mmol)	Solvent (THF/Diglyme)	Polymer yield (%)	Reaction Time (h)
1	8.62	8.62	0.122	Diglyme	40	48
2	8.62	8.62	0.061	Diglyme	35	48
3	8.62	17.2	0.122	THF	79	48
4	8.62	12.9	0.122	THF	77	48

4.2.4 Synthesis of Poly[bis(4- nitrobenzenamine)] phosphazene (PNBP)

PNBP was synthesized by the substitution reaction of PDCP with 4-nitroaniline in THF, in the presence of triethylamine under inert atmosphere. Polymer was obtained as a tacky pale yellow polymer with molecular weight 5742 and polydispersity index 1.42 (Figure.4.17).



Scheme 4.16: Synthesis of PNBP

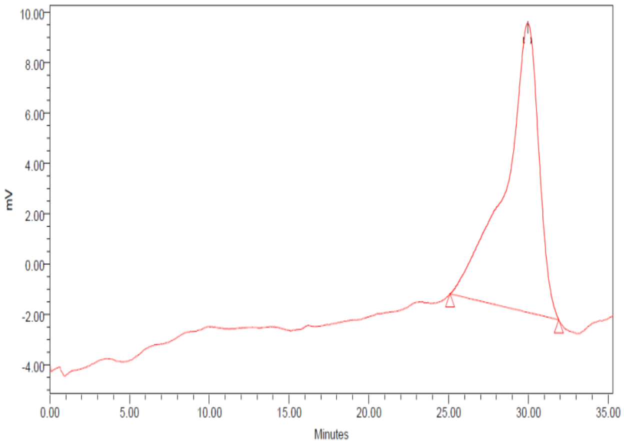


Figure 4.17: GPC trace of PNBP

The polymer PNBP was characterized by FT-IR Spectroscopy. FT-IR spectrum of the PNBP is shown in Figure 4.18. The major peaks are the absorption peaks around 1314, 1216 and 3200 cm^{-1}, which correspond to the phosphorous nitrogen bond (-P=N-) and –NH- of the aromatic amine. Absorption peak around 874 cm^{-1} is attributed to the -P-N- stretching vibration. In the IR spectrum, the peaks at 523 and 600 cm^{-1} due to the P-Cl absorption are present with less intensity which indicates that the substitution has not completely occurred and it may be due to the bulky nature of the substituent. Absorption around 1530 and 1380 cm^{-1} are of vibrations of the –NO_2 group. Absorption peaks around 2850 cm^{-1} is attributed to the methylene group.

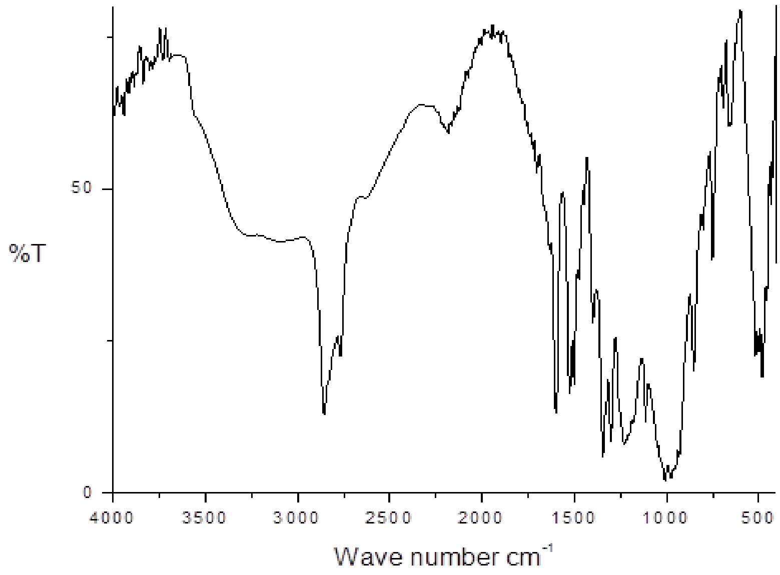


Figure 4.18: FTIR spectrum of PNBP

The formation of the polymer was confirmed by analyzing the ^{31}P and ^{1}H NMR spectrum recorded in $CDCl_3$. The ^{31}P NMR gives a broad signal at 12 ppm which is the characteristic peak of the PNBP and it showed a broad signal at -16 ppm which is attributed to the partially substituted phosphorous with nitro aniline in the polymer chain.The ^{1}H NMR spectrum of PNBP showed signals around 3.6, 6.2 and 7.5 ppm, which corresponded to the –NH- and aryl protons respectively. ^{13}C NMR spectrum exhibited chemical shifts at 113.4, 126.3, 139.0 and 152.5 ppm attributed to the various carbon atoms in the aromatic ring.

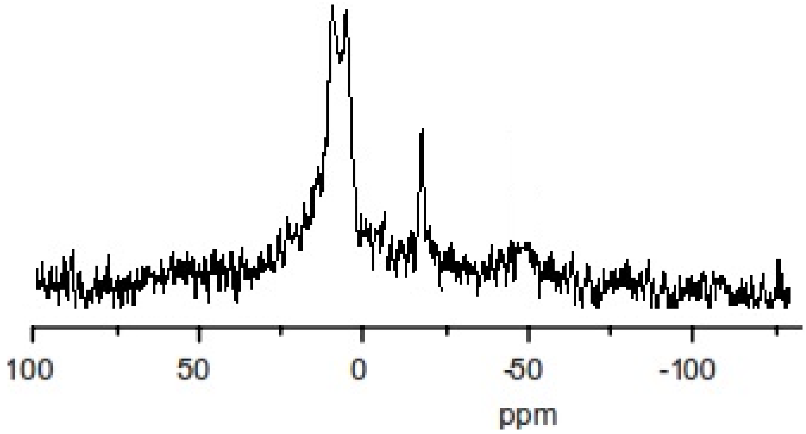


Figure 4.19: ^{31}P NMR spectrum of PNBP

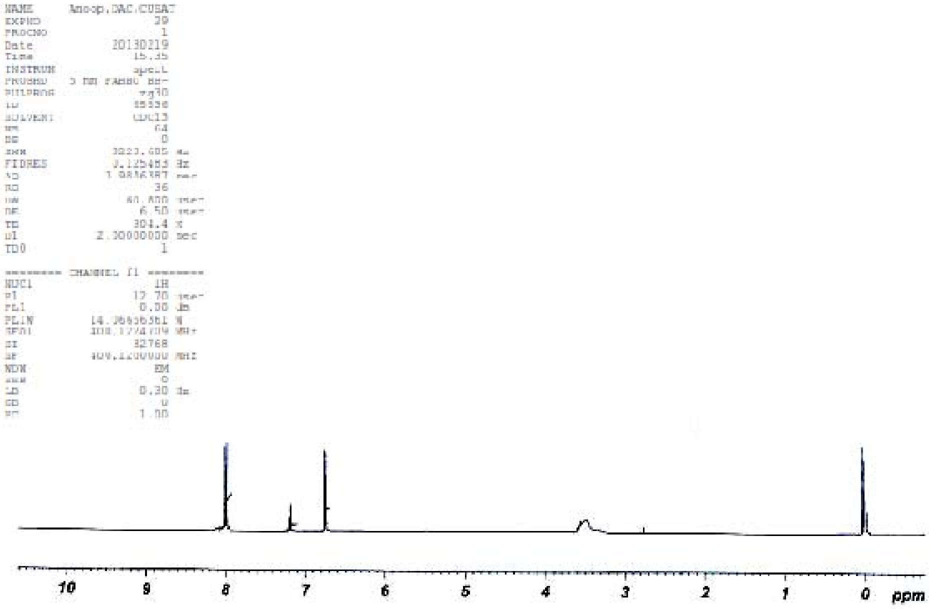
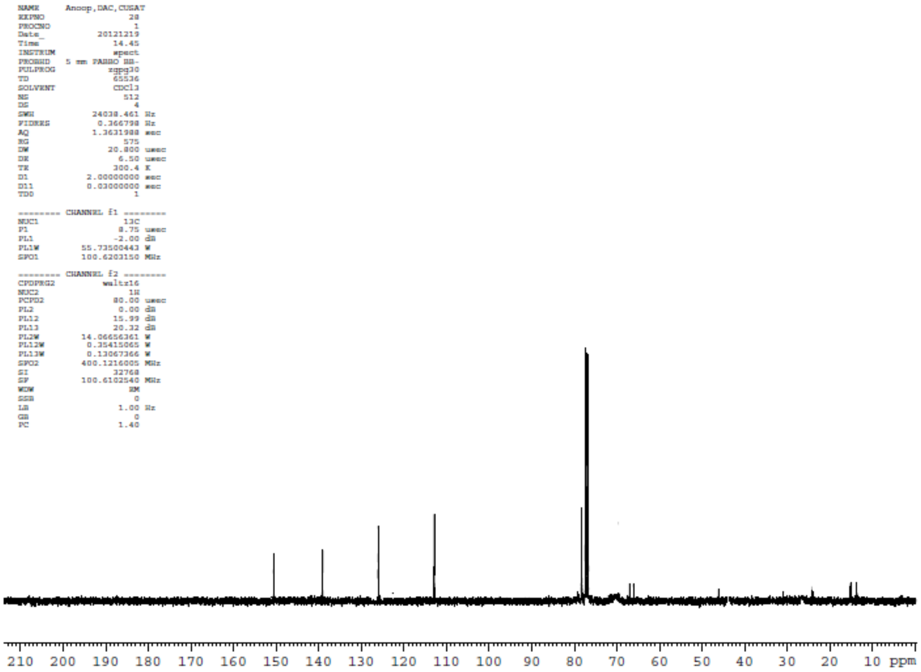


Figure 4.20: ^{1}H NMR spectrum of PNBP



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TE                  300.4 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

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PL1                 -2.00 dB
PL1W          55.73500443 W
SFO1         100.6203150 MHz

======== CHANNEL f2 ========
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PCPD2               80.00 usec
PL2                  0.00 dB
PL12                15.99 dB
PL13                20.32 dB
PL2W          14.06656361 W
PL12W          0.35415065 W
PL13W          0.13067366 W
SFO2         400.1216005 MHz
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SF           100.6102540 MHz
WDW                    EM
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Figure 4.21: ^{13}C NMR spectrum of PNBP

The thermal analysis of PNBP was performed by DSC and Figure 4.22 shows the results for a low temperature scan. The PNBPP showed glass transition temperature around -20 °C and the presence of bulky aromatic moiety restricted the segmental motion of the polymer chain and Tg moved to more positive value. The decomposition temperature of the PNBP was determined from a DSC thermogram at high temperature. The DSC scan of PNBP showed an exothermic peak in the temperature range 190-240 °C, with peak maximum at 230±5 °C and the exothermic decomposition is attributed to the elimination of $–NO_2$ group from the aromatic moiety.

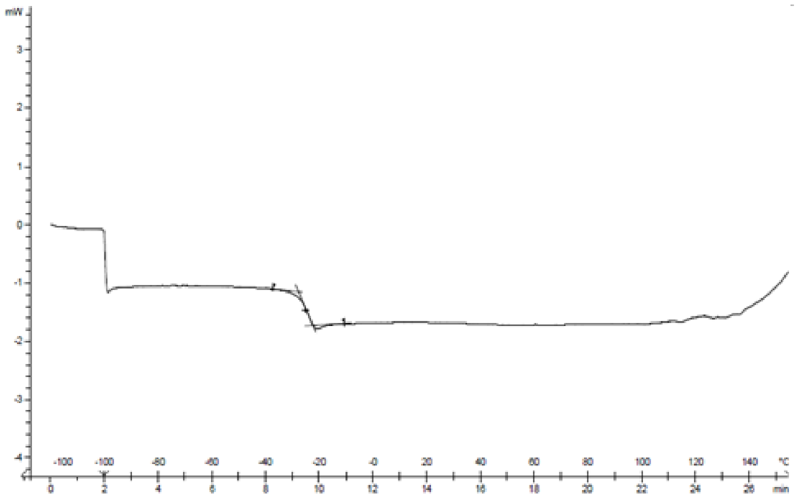
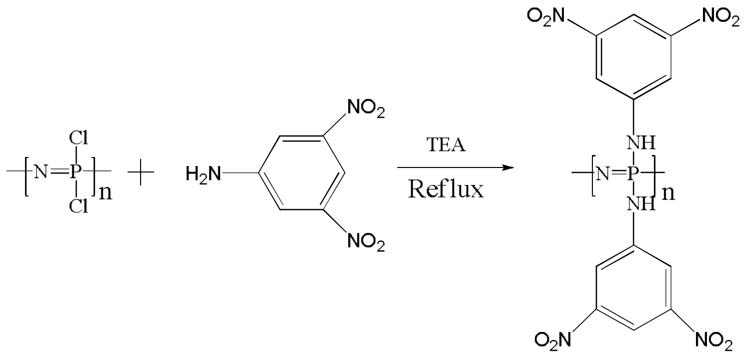


Figure 4.22: The DSC scan of PETFE

4.2.5 Synthesis of Poly [bis(3,5-dinitrobenzenamine)] phosphazene (PDNBP)

PDNBP was synthesized by the substitution reaction of PDCP with 3,5dintroaniline in THF, in the presence of triethylamine under inert atmosphere. The substituent dinitroaniline was prepared from 3,5 dintrobenzoic acid by Schimidt reaction using oleum and sodium azide. Polymer was obtained as a tacky yellow polymer with molecular weight 3880 and polydispersity index 1.66 (Fig.4.23).



Scheme 4.6: Synthesis of PDNBP

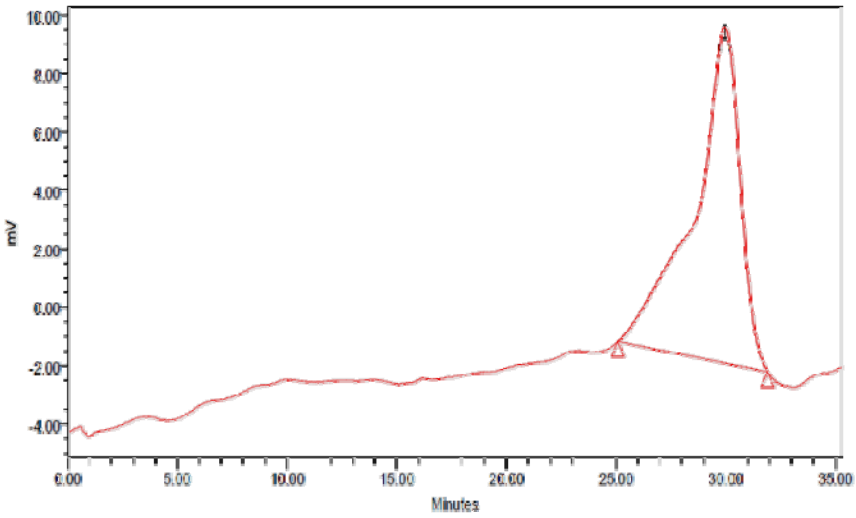


Figure 4.23: GPC trace of PDNBP

The polymer PDNBP was characterized by FT-IR spectroscopy. FT-IR spectrum of the PDNBP is shown in Figure 4.24. The major peaks are around 1314, 1216 and 3200 cm^{-1}, which correspond to the phosphorous nitrogen bond (-P=N-) and –NH- of the aromatic amine. Absorption peak around 874 cm^{-1} is attributed to the -P-N- stretching vibrations. In the IR spectrum, the peaks at 523 and 600 cm^{-1} due to the P-Cl absorption are present with less intensity which indicates that the substitution has not completely occurred and it may be due to the bulky nature of the substituent. Absorption around 1530 and 1380 cm^{-1} are attributed to the asymmetric and symmetric stretching vibrations of the $–NO_2$ group. Absorption peaks around 2850 cm^{-1} is attributed to the methylene group.

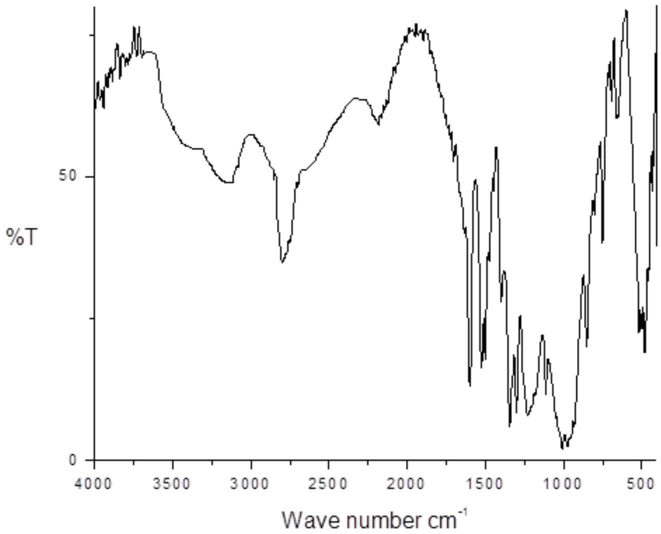


Figure 4.24: FTIR spectrum of PDNBP

The formation of the polymer was confirmed by analysing the ^{31}P, ^{1}H NMR and ^{13}C NMR spectra recorded in $CDCl_3$. The ^{31}P NMR spectrum gives a broad signal at 11 ppm which is the characteristic peak of the PDNBP and it showed a broad signal at -16 ppm which is attributed to the partially substituted polymer with dinitroaniline in the polymer chain. The ^{1}H NMR spectrum of PDNBP showed signals around 8.3, 7.68 and 4.4 ppm, which corresponded to the aryl protons and –NH- protons respectively. ^{13}C NMR spectrum showed signals of aryl carbon atoms at 156, 146, 114 and 112 ppm which confirmed the presence of aromatic moiety.

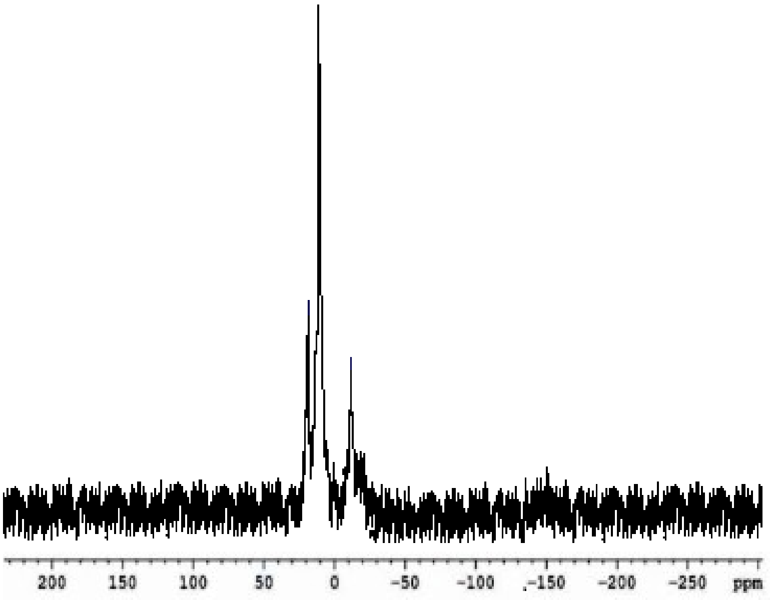
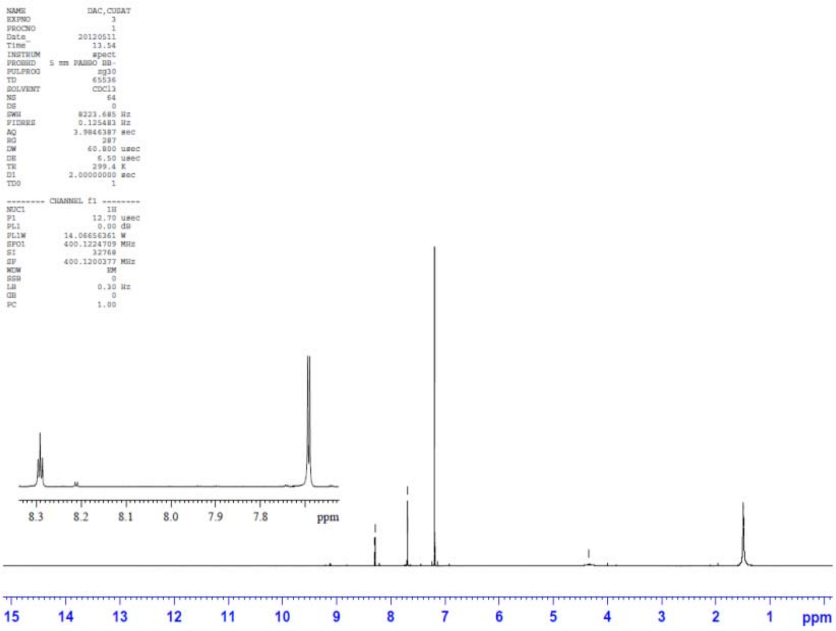


Figure 4.25: ^{31}P NMR spectrum of PDNBP



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Time                  13.54
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       64
DS                        0
SWH                8223.685 Hz
FIDRES             0.125483 Hz
AQ                3.9846387 sec
RG                      287
DW                   60.800 usec
DE                     6.50 usec
TE                    299.4 K
D1               2.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                    12.70 usec
PL1                    0.00 dB
PL1W            14.06656361 W
SFO1            400.1224709 MHz
SI                    32768
SF              400.1200377 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```

Figure 4.26: ^{1}H NMR spectrum of PDNBP

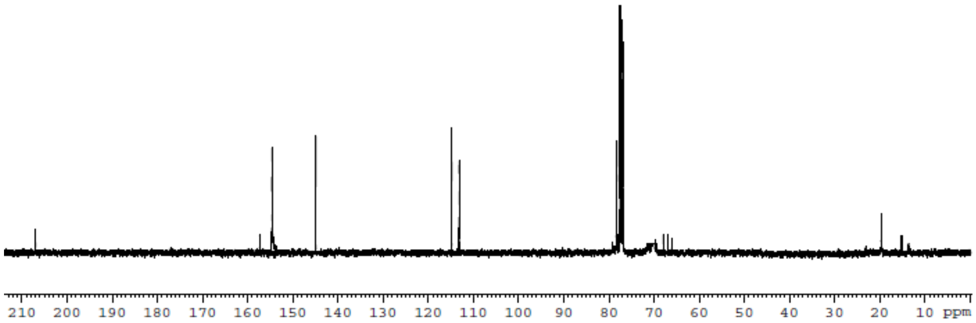

Figure 4.27: ^{13}C NMR spectrum of PDNBP

PDNBP is an yellow tacky and rubbery polymer. The thermal analysis of PDNBP was performed by DSC and Figure 4.28 shows the results for a low temperature scan. The PDNBPP showed glass transition temperature around -5 °C and it may be due to the restricted segmental motion of the polymer chain with bulky aromatic group. Here Tghas moved to more positive value and the DSC scan of PDNBP showed anexothermic peak in the temperature range 190-240 °C, with a maximum at 230 ± 5 °C and the exothermic decomposition is attributed to the elimination of nitro group from the aromatic moiety.

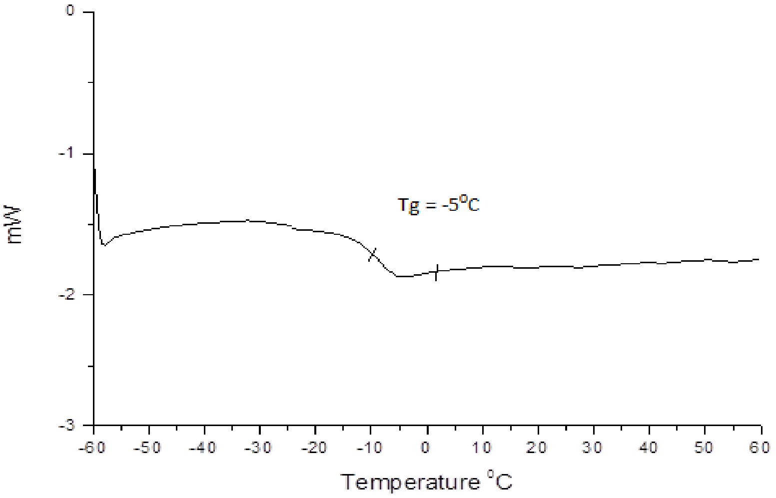

Figure 4.28: The DSC curve of PDNBP

4.3 Conclusion

Polyphosphazene with aliphatic and aromatic energetic groups in the side chain are successfully synthesized. Polyphosphazene based energetic polymers such as PTEP, PDNPP, PNBP and PDNBP were synthesized and characterized. Characterization technique such as ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, FT-IR, GPC and DSC were used.

4.4 Experimental

4.4.1 Synthesis of HCCTP

In a 250ml, 3 necked R.B flask equipped with a magnetic stirrer, thermometer, dropping funnel, 32.96 g (292 mmol) monochlorobenzene, 2.72g (50.8 mmol) of ammonium chloride, 0.0890 g (1.8 mmol) of zinc oxide and 1.073 g (8.31 mmol) of quinoline was taken. A solution of 13.74 g (66 mmol) phosphorus pentachloride in 32.96 g of monochlorobenzene which was heated to 100 ^{0}C was added over a period of 5 h to the flask at a temperature of 125-133 ^{0}C keeping solvent under refluxing. The reaction mixture was stirred under reflux for additional 2 h and cooled. The unreacted ammonium chloride was filtered off and the filtrate was distilled under reduced pressure to distil off the solvent and quinoline. The residue was extracted with hexane and the solvent was removed under vacuum to yield 85% HCCTP crystals.

4.4.2 Synthesis of PDCP

Freshly sublimed HCCTP 1 g (8.62 mmol) was placed in a dry pyrex tube and sealed under vacuum. The tube was placed in an oven and heated to 225 ^{0}C for 1 h and then at 250 ^{0}C for 16 h after which time, the molten material inside the tube almost ceased to flow. The tube was allowed to cool to room temperature, the contents was dissolved in a minimum amount of anhydrous

THF. The product, consisting of poly(dichlorophosphazene), was isolated as a colourless rubbery material upon precipitation into an excess of anhydrous hexane.

4.4.3 Solid state synthesis of PDCP

Under dry nitrogen atmosphere, 25 g (0.12 mol) PCl_5 powder was mixed with 3.53 g (0.027 mol) $(NH_4)_2SO_4$ in a one litre round bottomed flask equipped with a spin bar, a gas inlet and a reflux condenser.The reflux condenser was equipped with Tygon tubing which was immersed in a water bubbler at the other end.Under nitrogen atmosphere, the reaction vessel was placed in an oil bath pre-heated to 165 ^{0}C.Within 20 minutes all of the solid reactants liquefied signaling the completion of phase I of the overall polymerization reaction.The water bubbler was disconnected and the dry nitrogen atmosphere was re-established. The condenser was replaced with simple distillation head and temperature was raised gradually to 250 ^{0}C.The pale yellow product was stirred at this temperature for one hour, during which phosphoryl chloride liquid was distilled over and leaving behind a viscous, colourless liquid.The product was allowed to cool and purified by dissolving in minimum quantity of dry toluene and precipitation in dry hexane.The viscous liquid thus obtained was the product of polydichlorophosphazene. The yield of the polymer was found to be 70%.

4.4.4 Synthesis of PTEP

To a stirred solution of NaH, 0.62 g (25.8 mmol) in THF, 1.17 g (17.24 mmol) of trifluoroethanol dissolved in tetrahydrofuran was added over a period of 1h. A solution of PDCP 1 g (8.62 mmol) in THF was added after 3h. The reaction mixture was heated to reflux in the dark for 60 h in the presence of tetrabutylammonium bromide 0.5 g, (1.72 mmol) phase transfer catalyst. The reaction mixture was cooled, filtered and the solvent was removed under vacuum. The reaction mixture was poured into distilled water and the product was dried under vacuum. The polymer was dissolved in minimum quantity of dry acetone and precipitated in dry hexane and dried in vacuum. The polymeric product was isolated as a tackyoff white material withan yield of 75%.

4.4.5 Synthesis of PDNPP

To a stirred solution of freshly synthesized polydichlorophosphazene, 1.0 g (8.62 mmol)) in THF (20 ml), under an inert gas atmosphere, was added a solution of sodium salt of glycidol 1.66 g (17.2 mmol) in 10 ml THF along with catalyst TBAB 0.04 g (0.122 mmol).The mixture was heated to reflux and stirred for 18 h. Up on cooling to ambient temperature, the volume of THF was reduced and the concentrated solution was added to anhydrous hexane drop wise, with stirring. The precipitated polymer was dissolved in dichloromethane (50 ml) and washed with saturated brine solution (2 x 30 ml) and finally with water before drying over anhydrous $MgSO_4$. The $MgSO_4$ was filtered off and solvent was removed under vacuum. The polymer was dissolved in minimum quantity of dry acetone and precipitated in dry hexane and dried in vacuum. The polymeric product was isolated as a pale yellow viscous liquid with yield of 79%.

95% nitric acid (5 ml) was cooled, with stirring, to 0-5 ^{0}C in an ice/water bath. Glycidol substituted polyphosphazene (200 mg) in 2 ml dichloromethane was added drop wise and the reaction mixture was stirred for 15 minutes, maintaining the temperature below 5 ^{0}C. The solution was added drop wise with stirring, to cooled, distilled water yielding the nitrated product as a pale yellow oily precipitate. The precipitate was washed with several aliquots of distilled water and dried in vacuum at 50 ^{0}C for 2-3 h. The product was obtained as yellow viscous liquid and the yield was found to be 80%.

4.4.6 Synthesis of PNBP

To a stirred solution of freshly synthesized polydichlorophosphazene, 1.0 g (8.62 mmol) in THF (20 ml), under an inert gas atmosphere, was added a solution of 1.43 g (10.34 mmol) 4-nitroaniline in 10 ml THF. The mixture was heated to reflux and 1.44 ml (10.34 mmol) triethylamine was added and stirred for 18 h. Up on cooling to ambient temperature,the product was filtered through Whatman No.1 filter paper and the volume of the THF was reduced. The concentrated solution was added to 100 ml water with stirring. The precipitated polymer was dissolved in THF and was precipitated with dry hexane and dried in vacuum. The polymer isolated was an yellow, highly viscous liquid with an yield of 65%.

4.4.7 Synthesis of PDNBP

To a stirred solution of freshly synthesized polydichlorophosphazene 1.0 g (8.62 mmol) in THF (20 ml), under an inert gas atmosphere, was added a solution of 1.74 g (9.54 mmol) 3,5-dinitroaniline in 10 ml THF. The mixture was heated to reflux, 1.33 ml (9.54 mmol) triethylamine was added and stirred for 18 h. Up on cooling to ambient temperature, the product was filtered through Whatman No.1 filter paper and the volume of the THF was reduced. The concentrated solution was added to 100 ml water with stirring. The polymer was purified by precipitation from dry hexane and dried in vacuum. The polymer was isolated as a yellow highly viscous liquid with anyield of 60%.

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Chapter 5

BINDER PROPERTIES OF THE SYNTHESIZED POLYMERS

Abstract

Selection of energetic polymers as binders in rocket propellants and insensitive munitions is very important as it reflects in the final performance of the formulation. Heat of formation, glass transition temperature, molecular weight and oxygen balance etc. are key factors which ascertain the usefulness of polymers for binder applications. The heat of formation of both carbon based and phosphazene based energetic polymers were evaluated using bomb calorimeter. Oxygen balance of the polymers was calculated according to standard method. Glass transition temperature and molecular weights of the polymers were determined and correlated.

Keywords: Heat of formation, glass transition temperature, oxygen balance, binder properties.

5.1 Introduction

Modern high energy density materials such as RDX, HMX etc. are crystalline in nature and it is very difficult to make them as explosive charges in desired shapes. Hence energetic binders find application in explosive formulations. Apart from inert binders, currently energetic binders play a major role in rocket propellants and insensitive munitions. Main objectives of the use of binders are to make energetic formulation as insensitive munitions and also help them to get molded for explosive charges. An energetic polymer can act as excellent binder when it could meet certain criteria such as molecular weight control during synthesis, low glass transition temperature, energetic substituents in the polymer backbone, sufficient oxygen balance and heat of formation.

Obviously, apart from aforesaid qualities, mechanical properties also play vital role in the selection of energetic polymers as binders.

Azido polymers had received attention of researchers due to their positive heat of formation. But the carbon based energetic polymers had poor mechanical properties. To improve the mechanical properties, they were used in conjugation with energetic plasticizers of the same type. If curing was needed for the final matrix to improve mechanical properties and if the plasticizer was also hydroxyl terminated, it could further stiffen the matrix. The above problems could be solved by the use of polyphosphazene based energetic polymers, because polyphosphazenes are well known for their mechanical properties. Linear polyphosphazenes are synthesized which have are in low molecular weight and low glass transition temperature. Binder properties such as heat of formation, glass transition temperature, molecular weight and oxygen balance are determined.

5.2 Results and Discussion

Several polymeric binders have been synthesized in the past years to meet the specific requirements in aerospace and defense applications. Apart from mechanical properties, these polymers have to fulfill certain requirements such as

a) Low molecular weight

b) Low glass transition temperature

c) Good oxygen balance

d) Sufficient heat of formation.

5.2.1 Heat of Formation

The raw data obtained from the bomb calorimeter was used for the calculation of standard enthalpies of combustion and heat of formation [1-4]. The steps involved in these calculations are same for all the polymers. In general, this section includes an example of calculation for both oxetane and oxirane based energetic polymers [5-8] and polyphosphazene based energetic polymers [9-11].

Energetic polymers do not require any kindling agents as they undergo very neat combustion under high oxygen pressure, leaving negligible residue [12, 13]. The calorimetric determination was done on automatic Anton Parr static adiabatic Bomb Calorimeter. The calorimeter was calibrated using Parr thermochemical grade benzoic acid [14-17]. The steps involved in the calorimetric analysis are as such adopted for the evaluation of heat of formation of energetic polymers. Calculations were carried out on the assumption that 100% substitution of energetic groups occurred in the polymer backbone. To find out the standard heat of formation of products, NIST data key values [18] for thermodynamics were used (Table 1).

Table 1: NIST data key values for thermodynamics

Ideal combustion product	**$-\Delta H^0_f$ kJmol^{-1}**
CO_2(g)	393.51±0.13
H_2O(l)	285.83±0.04
N_2(g)	0
H_3PO_4(aq)	1299.0±1.5
HF(aq)	335.35±0.65

5.2.1.1 Heat of formation of GAP-THF diols

First step in the calculation after bomb calorimeter analysis was establishment of balanced equation for the empirical formula of the polymer monomeric unit. For GAP-THF diols, the balanced equation is,

$$\underset{(l)}{4C_7H_{13}N_3O_2} + \underset{(g)}{37\ O_2} \longrightarrow \underset{(l)}{26\ H_2O} + \underset{(g)}{28\ CO_2} + \underset{(g)}{6\ N_2}$$

$$\Delta n = (28+6) - 37 = 3$$

$$n = 0.170/171 = 0.001$$

The enthalpy of combustion is derived from the following equation,

$$\Delta H_c^o = \Delta U_c^o + \Delta nRT$$

Where $\Delta_c U^o$ is the standard internal energy of combustion,Δn is the difference in number of moles of gaseous products and reactants. R is universal gas constant and T is the absolute temperature.

$$q = C \times \Delta T$$

Where C is the heat capacity of bomb calorimeter and ΔT is the temperature increase in the calorimeter.

$$q = 8.456 \pm 2 \times 2.2$$

$$\Delta U_c^o = -q/n;$$

$$= -18.6032 \pm 4.4 / 0.001$$

$$= -18603.2 \pm 4.4$$

$$\text{So, } \Delta n = (28+6) - 37 = 3 \text{ mol and}$$

$$\Delta nRT = 3 \times 0.008314 \times 298$$

$$= 7.43$$

$$\text{Therefore, } \Delta H_c^o = (-18603.2 \pm 4.4) + 7.43$$

$$= -18595.76 \pm 4.4 \text{ kJ/mol}$$

In the next step, using the standard enthalpies of formation of the combustion products which are taken from the NIST data,$\Delta H_f^o$of polymer was calculated as follows,

$$\Delta H_f^o \text{ Polymer} = \square \Delta H_f^o \text{ (products)} - \Delta H_c^o \text{ Polymer}$$

$$= (26 \text{ x } -285.8) + (28 \text{ x } -393.5) - (-18595.76 \pm 4.4)$$

$$= 146.96 = 147 \pm 4.4 \text{ kJ/mol}$$

For oxetane and oxirane based polymers, the same method was used to evaluate the heat of formation (Table 2.)

Table 2: Enthalpy of formation of the synthesized polymers

Sl. No.	Polymer	Heat of formation in kJ/mol	Heat of formation in kCal/mol
1	GAP-THF	147	35
2	PDNPO	-1560	-373
3	PETEH	-3660	-875
4	BAMO-GLYN copolymer	87	21
5	BAMO-NMMO copolymer	25	6
6	GAP- BAMO copolymer	404	97

5.2.1.2 Heat of formation of PTEP

First step in the calculation after bomb calorimeter analysis was the establishment of a balanced equation for the empirical formula of the polymer monomeric unit. For the polymer PTEP, the balanced equation is,

$$4C_4H_4F_6O_2NP_{(s)} + 15\,O_{2(g)} \longrightarrow 16\,CO_{2(g)} + 10\,H_2O_{(l)} + 2N_{2(g)} + 4\,H_3PO_{4(l)} + 24\,HF_{(l)}$$

$$\Delta n = (16+2) - 15 = 3$$

$$n = 0.2452/243.04 = 0.001$$

The enthalpy of combustion is derived from thefollowing equation,

$$\Delta H_c^o = \Delta U_c^o + \Delta nRT$$

Where ΔU_c^o is the standard internal energy of combustion, Δn is the difference in number of moles of gaseous products and reactants. R is universal gas constant and T is the absolute temperature.

$$q = C \times \Delta T$$

Where C is the heat capacity of bomb calorimeter and ΔT is the temperature increase in the calorimeter.

$$q = 8.456 \pm 2 \times 2.3$$

$$= 19.45 \pm 4.6$$

$$\Delta U_c^o = -q/n;$$

$$= -19.45 \pm 4.6/ 0.001$$

$$\Delta U_c^o = -19277.23 \pm 4.6$$

$$\text{So, } \Delta n = (16+2) - 15 = 3 \text{ mol and}$$

$$\Delta nRT = 3 \text{ molx } 0.008 \times 298 \times 298$$

$$= 7.43$$

$$\text{Therefore } \Delta_c H^o = (-19277.23 \pm 4.6) + 7.43$$

$$= 19269.80 \pm 4.6 \text{ KJ/mol}$$

In the next step, using the standard enthalpies of formation of the combustion products which are taken from the NIST data, ΔH_f^o of polymer was calculated as follows,

$$\Delta H_f^o \text{Polymer} = \square \Delta H_f^o(\text{products}) - \Delta H_c^o \text{ Polymer}$$

$$= (10 \times -285.8) + (16 \times -393.5) + (4 \times -1299)$$

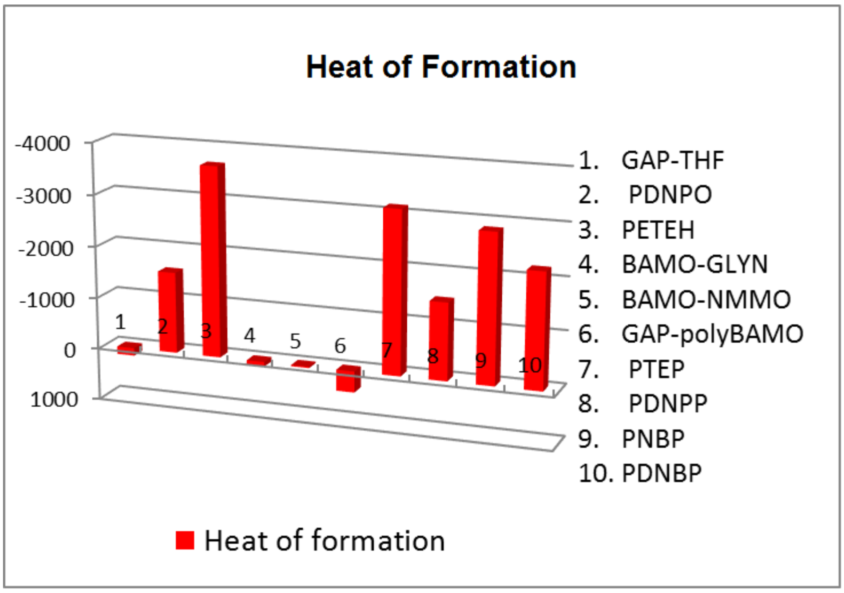
$$+ (24 \times -335.35) - (-19269.80)$$

$$= 3130.04 \text{ kJ/mol}$$

For the remaining polyphosphazene based polymers, the same method was used to evaluate the heat of formation (Table 3).

Table 3: Enthalpy of formation of the synthesized polymers

Sl. No.	Polymer	Heat of formation in kJ/mol	Heat of formation in kCal/mol
1	PTEP	-3130	-748
	PDNPP	-1480	-353
2	PNBP	-2856	-683
3	PDNBP	-2212	-529



From the bar diagram it is clear that the polymers which contain azide groups have positive heat of formation and the polymer GAP-polyBAMO shows highest positive heat of formation among them. Apart from azide containing polymers, PDNPO and PDNPP have good heat of formation among the carbon based and phosphazene based polymers.

5.2.2 Oxygen Balance

Since most of the energy release comes from oxidation reactions, the amount of oxygen available is a critical factor. If there is insufficient oxygen to react with the available carbon and hydrogen, the explosive is considered to be oxygen deficient. The converse is considered oxygen rich. If an explosive molecule contains just enough oxygen to form carbon dioxide from carbon, water from hydrogen , sulfur dioxide from sulfur, and all metal oxides from metals with no excess, the molecule is said to have a zero oxygen balance [19-20]. The molecule is said to have a positive oxygen balance if it contains more oxygen than is needed and a negative oxygen balance if it contains less oxygen than is needed; the combustion will then be incomplete and large amount of toxic gases like carbon monoxide will be present.

The oxygen balance is calculated from the empirical formula of a compound in percentage of oxygen required for complete conversion of carbon to carbon dioxide, hydrogen to water, and metal to metal oxide.

The procedure for calculating oxygen balance [21] in terms of 100 grams of the explosive material is to determine the number of moles of oxygen that are excess or deficient for 100 grams of a compound.

$$OB\% = \frac{-1600}{Mol.wt.of compound} \times (2X + (Y/2) + M - Z)$$

Where X = number of atoms of carbon, Y = number of atoms of hydrogen, Z = number of atoms of oxygen, and M = number of atoms of metal (metallic oxide produced).

As a general rule, the oxygen balance should be near zero to get the maximum amount of energy release. Other concerns like stability or volatility often limit the oxygen balance for chemical compounds. TNT is an example of a relatively powerful explosive that is oxygen deficient.

Some explosives are mixtures of chemicals that do not react and are known as *composites*. A common example is composite B-3 which is made up of a 64/36 mixture of RDX ($C_3H_6N_6O_6$) and TNT. If written in the same notation, it would be $C_{6.851}H_{8.750}N_{7.650}O_{9.300}$ and would have an oxygen balance, OB = -40.5%. ANFO which is a 94/6 mixture of ammonium nitrate and fuel oil has a -0.6% oxygen balance. Composite explosives generally have oxygen balances that are closer to the ideal case of zero.

In the case of TNT ($C_6H_2(NO_2)_3CH_3$),

Molecular weight = 227.1

X = 7 (number of carbon atoms)

Y = 5 (number of hydrogen atoms)

Z = 6 (number of oxygen atoms)

Therefore

$$OB\% = \frac{-1600}{227.1} \times (14 + 2.5 - 6)$$

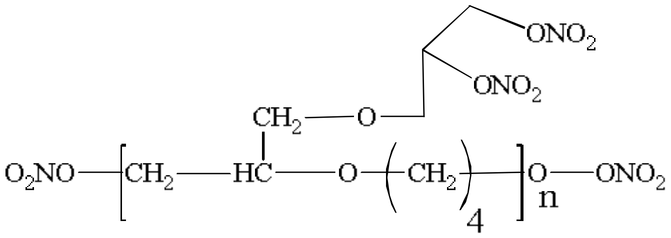
OB% = -74% for TNT

One area in which oxygen balance can be applied is in the processing of mixtures of explosives. The family of explosives called amatols are mixtures of ammonium nitrate and TNT. Ammonium nitrate has an oxygen balance of +20% and TNT has an oxygen balance of −74%, so it would appear that the mixture yielding an oxygen balance of zero would also result in the best explosive properties. In actual practice a mixture of 80% ammonium nitrate and 20% TNT by weight yields an oxygen balance of +1%, the best properties of all mixtures, and an increase in strength of 30% over TNT.

Examples of materials with negative oxygen balance are e.g. trinitrotoluene (-74%), aluminium powder (-89%), sulfur (-100%), or carbon (-266.7%). Examples of materials with positive oxygen balance are ammonium nitrate (+20%), ammonium perchlorate (+34%), potassium chlorate (+39.2%), sodium chlorate (+45%), sodium nitrate (+47%), tetranitromethane (+49%), lithium perchlorate (+60%), or nitroglycerine (+3.5%).

Commercial explosive materials should have oxygen balance close to zero, in order to minimize the production of nitrogen oxides and carbon monoxide; the gaseous products of incomplete combustion are especially dangerous in confined spaces.

5.2.2.1 Oxygen balance of PDNPO



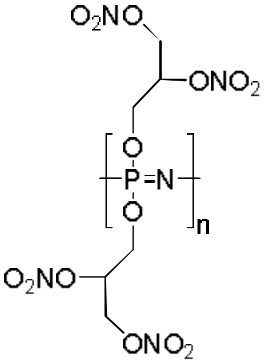
Molecular formula of the repeating unit is $C_{10}H_{18}O_9N_2$

Molecular weight = 274

Oxygen Balance = -1600 / 274 (2 x 10 + (18/2) -9)

= -117 %

5.2.2.2 Oxygen balance of PDNPP



Molecular formula of the repeating unit is $C_6H_{10}O_{14}N_5P$

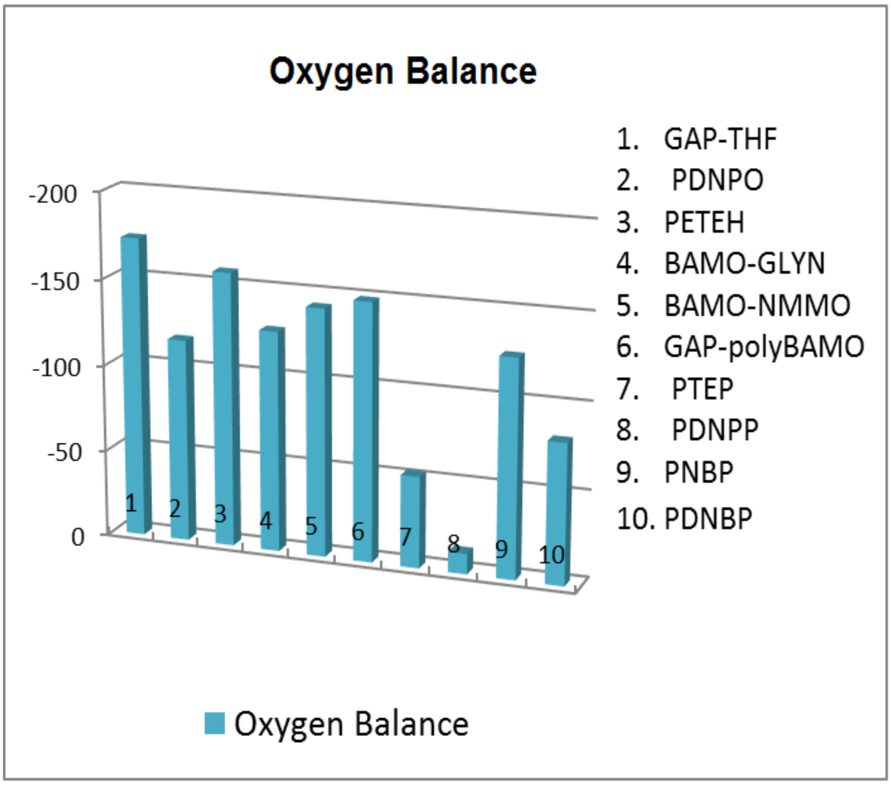
Molecular weight = 407

Oxygen Balance = -1600 / 407 (2 x 6 + (10/2) -14)

= -12 %

Table 4: Oxygen balance of the synthesized polymers

Sl.No.	Polymer	Oxygen Balance (%)
1	GAP-THF	-173
2	PDNPO	-117
3	PETEH	-158
4	BAMO-GLYN Copolymer	-127
5	BAMO-NMMO Copolymer	-143
6	GAP-BAMO Copolymer	-149
7	PTEP	-53
8	PDNPP	-12
9	PNBP	-125
10	PDNBP	-81



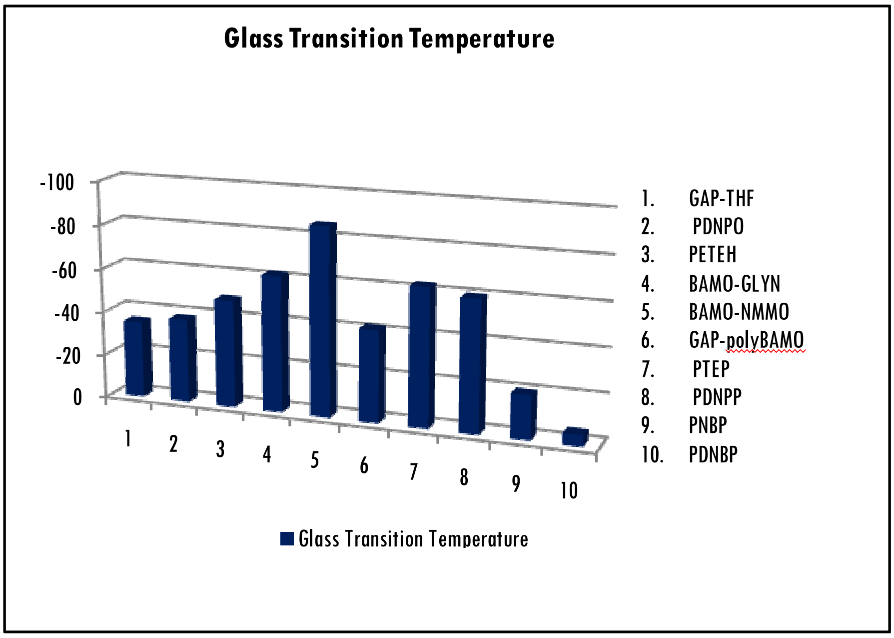
The polymer PDNPP has higher oxygen balance nearing to zero among others, which is an essential criterion for the new generation enrgetic polymers or plasticizers for binder applications. If the polymers have substantial oxygen balance, the amount of oxidiser used in the final formulation can be reduced there by improving the mechanical properties of the final formulation. Currently used oxidisers such as ammonium nitrate in combination with ammonium perchlorate in high ratio is found to exhibit tailing while combustion, which is a major drawback. So by the use of energetic polymers with significant oxygen balance, the ratio to the explosive formaion can be increased since these polymers have good oxygen balance and energy content.

5.2.3 Glass transition temperature

Tg is the temperature at which an amorphous polymer passes fromthe glassy state to rubbery state. The glass transition temperature is a function of chain flexibility [22-25]. The glass transition occurs when there is enough vibrational (thermal) energy in the system to create sufficient free-volume to permit sequences of polymer chain to move together as a unit. At this point, the mechanical behavior of the polymer changes from rigid and brittle to a tough and leathery.

Actually, the glass transition temperature is more important in plastic applications than is the melting point, because it gives an idea about how the polymer behaves under ambient conditions. The melting temperature is often referred to as the "first-order transition" --- that's where the polymer changes state from solid to liquid. Technically, only crystalline polymers have a true melting point; that's the temperature at which the crystallites melt and the total mass of plastic becomes amorphous. Amorphous polymers do not have a true melting point, however, they do have a second-order transition where their mechanical behaviorchanges from a glassy nature to viscous rubbery flow.

If the Tg is well below room temperature, the material is what is commonly termed as a rubber or elastomer which is soft and easily stretched; [26-29] and those materials whose Tg is reasonably close to the ambient temperature will exhibit plastic material behavior which is strong and tough with good impactresistance.



	GAP-THF	PDNPO	PETEH	BAMO-GLYN	BAMO-NMMO	GAP-polyBAMO	PTEP	PDNPP	PNBP	PDNBP
Glass Transition Temperature	-35	-38	-49	-62	-86	-42	-63	-60	-20	-5

It is clear from the above graph that Tg values of the polymers gradually decreased with increasing the size of the substituent on the backbone. Inclusion of aromatic energetic groups in polyphosphazene changed the Tg values to more positive than others. Apart from the size of the substituent, the percentage of substitution and molecular weight also has great influence on Tg values. This may be the reason why some polymers exists as tacky material at ambient temperature while others exist as viscous liquid. From the density measurements also it is clear that bulky group substituted polymers and higher molecular weight polymers have high densities where the segmental motion is restricted.

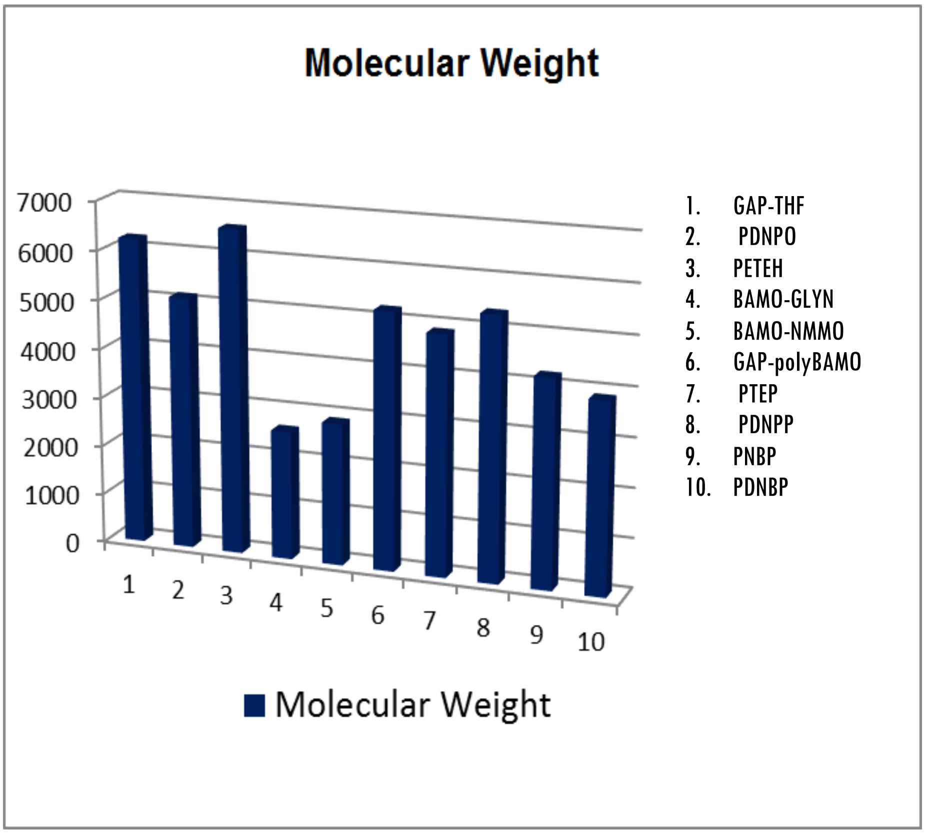
5.2.4 Molecular weight

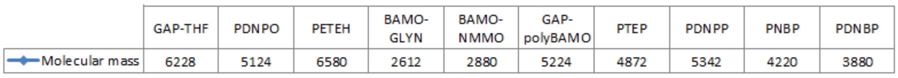
Molecular weight of the polymers was determined by GPC using THF as mobile phase and is shown in Table 4. $\overline{Mn}$, the number average molecular weight, which is the ratio of the total weight of the polymer to the total number of molecules present. But $\overline{Mw}$, the weight average molecular weight is the mean value of the weight distribution of molecular sizes. $\overline{Mn}$ can be determined easily and it has become the more often used molecular weight average [30].

Number average molecular weight is important in the case of low molecular weight species because $\overline{Mn}$ counts the number of molecules present rather than the weight of the polymer. In the case of polymer mixtures, low molecular weight polymer contributes little to $\overline{Mw}$ and high molecular weight to large extent. Polydispersity index is a measure of the width of molecular weight distribution (MWD) and is theoretically important.

A well-defined narrow molecular weight distribution is obtained if PDI is close to 1. The incorporation of monomer units in to the growing polymer chain during polymerization obeys certain statistical principles. As a result the reaction is heterogeneous at its molecular level and molecular properties vary throughout the polymer sample with corresponding frequencies of molecules bearing those property values.

In the present case majority of the synthesized polymers have low molecular weight, preferably, $\overline{Mn}$ below 5000 and are amenable for the binder applications, since glass transition temperature of the polymers depended on the molecular weights. Due to low molecular weights, the polymers either exist as highly viscous liquid or as tacky material which avoids the chemical crosslinking agents in the final energetic formulations. The following bar diagram shows the number average molecular weights of the synthesized polymers and it can be observed that most of the polymers have molecular weights within 2500- 5500 range which are either oligomers or polymers.





	GAP-THF	PDNPO	PETEH	BAMO-GLYN	BAMO-NMMO	GAP-polyBAMO	PTEP	PDNPP	PNBP	PDNBP
Molecular mass	6228	5124	6580	2612	2880	5224	4872	5342	4220	3880

5.3 Conclusion

Binder properties, which are crucial for the selection of energetic polymers and plasticizers in binder applications, such as heat of formation, molecular weight, and glass transition temperature and oxygen balance were evaluated and discussed.

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Chapter 6

SUMMARY AND CONCLUSIONS

Abstract

Current technology utilizes cast cured polymer bonded explosives (PBX) for military applications with energetic polymers, plasticizers, fillers, oxidizers and energetic materials. The energetic polymers and plasticizers form chemical crosslinks with explosives and for that, curing is needed, which stiffens the matrix and renders them difficult to manipulate. Practice of twin screw extrusion or injection molding technology for solid energetic materials with novel energetic binders which do not require chemical crosslinking helps to overlay the aforesaid difficulties. Both carbon based and polyphosphazene based energetic polymers were synthesized, among these carbon based polymers are low molecular weight polymers and are hydroxyl terminated which needs chemical crosslinking to wrap explosive charges. But the polyphosphazene based energetic binders are tacky or rubbery in nature which do not require any chemical crosslinking agents. Here the essential requirements of polymers for binder applications have been discussed along with future outlook also.

Keywords: *Energetic Polymers, Energetic Plasticizers, Polyphosphazene.*

6.1 Introduction

Modern weapon systems and rocket propellants are being developed world wide in these days. These energetic materials are envisaged to perform as insensitive materials with enhanced energy output, comply with safety and environmental aspects and low cost of production. The use of energetic polymers and plasticizers as energetic additives as well as binder is one of the practical ways to get insensitive munitions and high energy output during demilitarization.

The present work has emphasized on the synthesis and characterization of both carbon based and polyphosphazene based energetic polymers. Binder properties such as molecular weight, glass transition temperature, oxygen balance and heat of formation of these polymers were evaluated and discussed.

6.2 Summary

The thesis was divided in to six chapters and chapter wise arrangement of the thesis is as follows.

First chapter depicted the brief history of energetic polymers and the brief literature survey of energetic polymers based on oxetanes and oxiranes. It also dealt with the history of energetic plasticizers and energetic polyphosphazenes. Various characterization techniques adopted for the current study and the main objectives of the present work were discussed in chapter 1.

Second chapter included the synthesis and characterization of oxetane based energetic polymers. It also included the synthesis of PECH diol and PECH-THF diol and their characterization. The synthesis of GAP-THF diols, poly(dinitropropanoxy)oxirane (PDNPO) and poly(bistrifluoroethoxy)oxirane (PBTEO) by attaching energetic groups such as azido, nitrato and fluoro to the polymer backbone and their characterization were discussed.

Third chapter has emphasized on the synthesis and characterization of copolymers of both oxetanes and oxiranes. Here three copolymers such as BAMO-GLYN copolymer, BAMO-NMMO copolymer and GAP-BAMO copolymer were synthesized and characterized. BAMO-GLYN copolymer was synthesized by the cationic ring opening polymerization between the monomer

BAMO and GLYN and BAMO-NMMO copolymer was synthesized by the copolymerization between BAMO and NMMO. But GAP-BAMO was synthesized by the ring opening polymerization between epichlorohydrin (ECH) and bischloromethyloxetane (BCMO) followed by azidation. These polymers were also characterized.

Fourth chapter has dealt with the synthesis and characterization of novel energetic polyphosphazenes. The precursor polydichlorophosphazene was synthesized and fluoro, nitrato, mono nitroaromatic amines and dinitroaromatic amines were attached to get the polymers PTEP, PDNPP, PNBP and PDNBP. All the polymers were characterized.

Fifth chapter has focused on the binder properties of the synthesized polymers. The binder properties such as heat of formation, glass transition temperature, molecular weight and oxygen balance were evaluated and discussed.

Last chapter is the summary of the investigations and the conclusions drawn from the earlier chapters and future outlook.

6.3 Conclusion

The major conclusions that were drawn from the present work are the following:

1) Synthesis of high molecular weight PECH-THF diol with low Tg could be achieved with classical cationic polymerization technique without a polyol which would help to avoid unwanted crosslinking during curing.
2) Successfully incorporated energetic moieties such as fluoro, nitrato and azido groups in to the polymer which was obtained by ring opening polymerization of oxiranes.

3) Achieved the synthesis of low molecular weight copolymers of both energetic oxirane and oxetane monomers. These polymers were energetically rich as it contained both azido and nitrato groups when compared to energetic homo polymers.
4) Synthesized novel polyphosphazene based energetic polymers having nitrato and fluoro energetic groups which were rubbery and tacky in nature. Achieved the synthesis of polyphosphazene having nitroaromatic amines by the condensation reaction between mononitramine and dintramine with polydichlorophosphazene. This made them suitable for use effectively in injection moulding or twin screw extrusion with solid energetic materials.
5) Ascertained which polymer would perform as a good binder in rocket propellants and explosive formulation based on the heat of formation, glass transition temperature, oxygen balance and molecular weight of the polymers.

From the oxirane based energetic polymers synthesized, GAP-THF was found to exhibit positive heat of formation with substantial molecular weight and PDNPO was also a good candidate since it has good oxygen balance and energy content.

Among the copolymers, BAMO-GLYN copolymer showed good capability to act as a binder because it was energy rich, had average oxygen balance, low Tg and good number average molecular weight.

Among polyphosphazene based energetic polymers, the polymer PDNPP could be the best to be used as energetic binder. It has good heat of formation, low Tg, low molecular weight and better oxygen balance.

6.4 Future Outlook

Development of high energy materials is an emerging field. But most of these materials are solids and in order to make them act as insensitive munitions, efficient binder has to be used. So large extent of research is going on in the field of energetic polymers and plasticizers in order to develop effective binders. Polyphosphazene based energetic polymers are the entry level polymers to act as binders. Polyphosphazenes are well known for their mechanical properties and when they become energetic, they will be the better ones compared to other binders which are currently used. So the design of future weapon system having solid energetic materials would be wrapped with energetic polyphosphazene for better and safe performance. If we could introduce more energetic groups in the polyphosphazene, it can be used as insensitive munitions itself and can be added in to explosive charges where we need fillers, oxidisers or binders. If highly energetic aromatic moiety can be incorporated in to the polyphosphazene having amino or hydroxyl functional groups will be a great breakthrough. Similarly, introduction of energetic oligomers as branches in polyphosphazene will perform well in future explosive charges.