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Energetic Polymers and Plasticisers for Explosive Formulations - A Review of Recent Advances

Arthur Provatas

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Weapons Systems Division
Aeronautical and Maritime Research Laboratory

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ABSTRACT

In an effort to comply with Insensitive Munitions (IM) criteria, energetic binders comprising polymer and plasticiser(s) are finding use in cast-cured polymer bonded explosives and cast composite rocket propellants. Energetic binders can be considered as cross-linked polymers that provide a matrix to bind explosive ingredients together with a plasticiser. Once cured, the polymeric binder is a tough elastomeric rubber capable of absorbing and dissipating energy from hazardous stimuli, lending itself well to IM applications. This general document outlines the most promising energetic polymers and plasticisers being considered today.

Attention is focussed on several energetic polymers including glycidyl azide polymer, GAP, poly(3-nitratomethyl-3-methyloxetane), polyNIMMO and poly(glycidyl nitrate), polyGLYN, although several other energetic polymers will also be reviewed. Energetic plasticisers including oligomers (low molecular weight) of the polymers mentioned above, as well as a variety of nitrate esters, nitroaromatics and azido plasticisers, will also be reviewed. Finally, the review will recommend binder systems for DSTO's future energetic binder programs.

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Executive Summary

In an effort to comply with Insensitive Munitions (IM) criteria, energetic binders comprising polymer and plasticiser(s) are being used in cast-cured polymer bonded explosives and cast composite rocket propellants. These new energetic binder systems offer energy output increases over conventional 'inert' non-energetic binder systems and are thus of important consequence to the ADF. This report outlines the most promising energetic polymers and plasticisers being considered by Defence forces around the world.

Energetic binders are polymers which crosslink explosive ingredients together with a plasticiser into a tough yet flexible three-dimensional network. Plasticisers are typically added both to facilitate processing and to improve mechanical properties of the final cured formulation.

This review comprises two main sections. The first section examines the synthesis, properties, and polymerization chemistry of energetic polymers while the second section is concerned with the chemistry of energetic plasticisers and their role in energetic binder systems.

This report reviews recent developments in energetic binder systems (both polymers and plasticisers) for use in advanced cast-cured explosive and propellant formulations, and recommends binder systems that might best address the future requirements of the ADF.

Authors

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Weapons Systems Division

Arthur Provatas graduated with a PhD (Chem. Tech.) from the University of South Australia in 1997 in polymer chemistry. During 1995, he interrupted his PhD studies to travel to the USA, as part of a joint Dow Corning-UniSA visiting fellowship to investigate advanced copolymers made by interfacial polymerization. US patents have been awarded to this research. His multidisciplinary research has led him to publish research in inorganic chemistry, chemical engineering, polymer science, surface chemistry and organic synthesis. In 1998 he commenced work for the Explosives Group of DSTO. The focus of his research at DSTO resides with energetic polymers as binders for military applications and polymer bonded explosives.

Contents

GLOSSARY

GLOSSARY

Abbreviations/ Acronyms	**Name**
BAMO	3,3-Bis(3-azidomethyl)oxetane
BDNPA	Bis-(2,2-dinitropropyl) acetal
BDNPF	Bis-(2,2-dinitropropyl) formal
BDNPA/F	Eutectic mixture of BDNPA and BDNPF
BuNENA	Butyl-2-nitratoethyl nitramine
BTTN	1,2,4-Butanetriol trinitrate
DBTDL	Dibutyltin dilaurate
DSC	Differential Scanning Calorimetry
ECH	Epichlorohydrin
EtNENA	Ethyl-2-nitratoethyl nitramine
GAP	Glycidyl azide polymer
GAPA	Azido-terminated glycidyl azide polymer
GLYN	Glycidyl nitrate
HTPB	Hydroxyl terminated polybutadiene
HMX	Cyclotetramethylenetetranitramine
IM	Insensitive Munitions
IPDI	Isophorone diisocyanate
Isp	Specific impulse
LOVA	Low Vulnerability Ammunition
MeNENA	Methyl-2-nitratoethyl nitramine
Mn	Number average molecular weight
mp	Melting point
Mw	Weight average molecular weight
NENA	Nitrato ethyl nitramine
NHTPB	Nitrated hydroxyl terminated polybutadiene
NMMO	2-Nitratomethyl-3-methyloxetane
PBX	Polymer Bonded Explosive
PECH	Polyepichlorohydrin
polyGLYN	Polymer of 2-nitratomethyloxirane
polyNIMMO	Polymer of 3-nitratomethyl-3-methyloxetane
RDX	Cyclotrimethylenetrinitramine
Tg	Glass transition temperature
Tm	Melting temperature
TMETN	Trimethylolethane trinitrate
TPE	Thermoplastic Elastomer

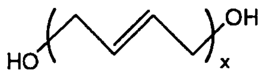
1. Introduction

The design of future weapons systems requires the use of explosive and propellant formulations having enhanced performance (energy output) and reduced vulnerability during storage and transportation. Several important design considerations for such formulations include improved mechanical properties, decreased signature, extended service life and reduced environmental impact in manufacture, use and disposal.

In particular, extensive programmes have evolved worldwide for the development and introduction of Insensitive Munitions (IM), ordnance that fulfils performance expectations but in which the response to unplanned hazardous stimuli is reduced. Australia has a policy (DI(G) LOG 0-10) for introduction of IM into the ADF inventory, as it is practical, sensible and cost-effective to do so. Several approaches are available to provide IM solutions, including weapon design, mitigation devices and packaging, although perhaps the most obvious is the use of intrinsically less sensitive explosive and propellant formulations.

One approach to less sensitive explosives is the development of cast-cured polymer bonded explosives (PBX), in which the explosive ingredient is suspended in a polymeric binder, cured in-situ as a tough elastomeric rubber which absorbs and dissipates the energy from hazardous stimuli. Binders are typically cross-linked polymers providing a matrix to bind the solids together with a plasticiser (usually not more than 50% of the total binder system) to ease processing of the uncured mix and to modify the mechanical properties of the final composition.

One of the earliest binders used in energetic materials was a mixture of nitrocellulose and nitroglycerine, where the nitrocellulose was used to thicken the nitroglycerine and reduce impact and friction sensitivity [1]. Nowadays, the current practice is to encapsulate the explosive in a binder, composed of a polymer such as hydroxy-terminated polybutadiene (HTPB) crosslinked with isocyanates, and containing a plasticiser such as dioctyl adipate (DOA). Other polymers include carboxy-terminated polybutadiene (CTPB) and hydroxy-terminated polyethers (HTPE) [2].



HTPB

These 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. For example, HTPB requires a theoretical solids loading of 92% by weight of ammonium perchlorate for complete combustion, but 15-20% of binder is required to prepare a processable formulation. 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 extrusion or pressing, thereby reducing the quantity of inert binder required. Another approach has been to use polymers and/or plasticisers 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 plasticiser. Incorporation of these explosophores increases the internal energy of the formulation, in addition to improving the overall oxygen balance.

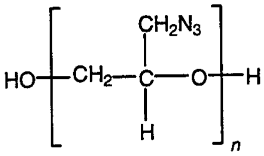
New energetic binders that appear to offer such promise include azide functional polymers like glycidyl azide polymer (GAP), or the nitrato polyethers like poly(3-nitratomethyl-3-methyloxetane) (polyNIMMO), and poly(glycidyl nitrate) (polyGLYN). [Monomers are NIMMO, 3-nitrato-methyl-3-methyloxetane and GLYN, glycidyl nitrate, respectively]. Other energetic binders discussed in this report include fluoropolymers, polyvinylnitrates, polynitroaromatics, *N,N*-bonded epoxy functional polymers, and nitrated polybutadienes like NHTPB. Energetic plasticisers include oligomers of the polymers mentioned above, as well as a wide variety of nitrate esters, nitroaromatics and azido plasticisers.

This report reviews recent advances in the development of energetic polymers and plasticisers for use in advanced cast-cured explosive and propellant formulations, and recommends ingredients that might best address the future requirements of the ADF. The report is split into 2 chapters, the first chapter examines energetic polymers while the second chapter reviews the plasticisers before making any recommendations.

2. Energetic Polymers

2.1 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 [1]. 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) [3].



$HO-[CH_2-CH(CH_2N_3)-O]_n-H$

GAP

GAP was first synthesised in 1972 by Vandenburg [4] by the reaction of sodium azide in dimethylformamide with the polyepichlorohydrin, PECH-triol. Frankel and co-workers at Rocketdyne [5] synthesised PECH-triol by polymerization of epichlorohydrin (ECH) with glycerol as the initiator unit, as shown below in Figure 1. GAP may then be crosslinked by reaction with isocyanates to give an extended polymeric matrix.

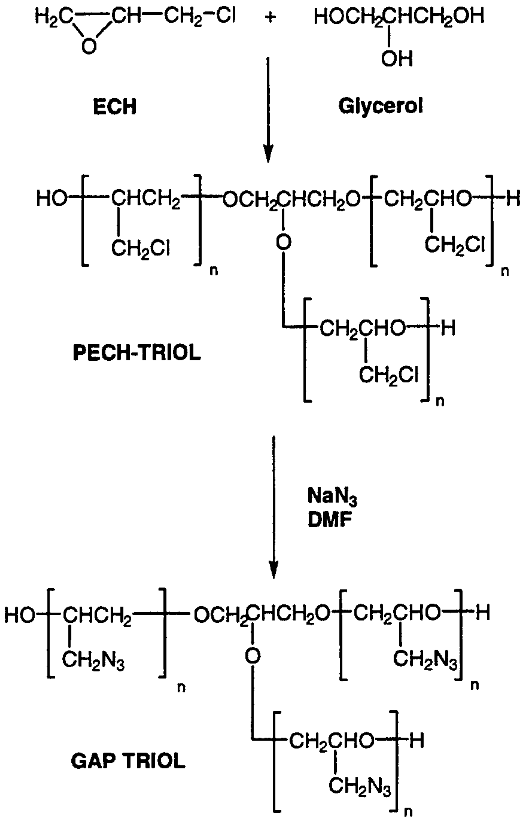
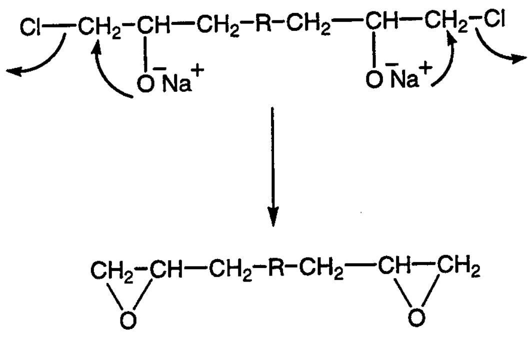


Figure 1: Synthesis of GAP Triol

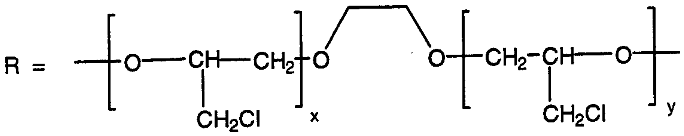
This general process can also be used to produce linear GAP-diol and branched GAP-diol polymers [6]. The first step of the process can actually be by-passed, as commercial quantities of PECH-diol are available. Optimization of PECH production has led to the successful development of a process which yields 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 [7], organic solvent [6] or in polyethylene oxide [8].

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. Ampleman has patented a method of synthesising GAP with increased functionality, by regiospecific epoxidation of linear PECH under basic conditions [9]. Subsequent opening of the epoxides under different conditions leads to PECH polymers with different functionalities and structures depending on the reactants. Since the azidation step does not change the functionality of PECH (direct replacement of Cl by N_3), Ampleman conceived the novel idea of changing the functionality of PECH under mild basic conditions, where PECH with terminal alcoholate groups are formed, and which then react with the chloride groups to give the epoxy functionalised PECH.

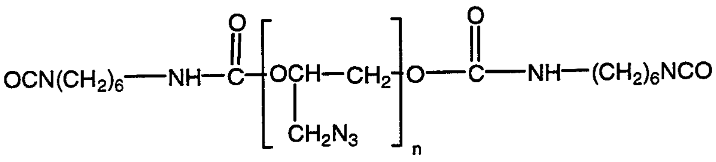
The mechanism for the epoxidation step can be shown as:



where,



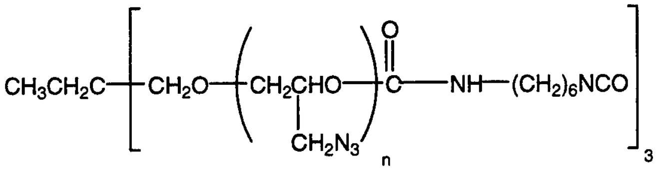
The next stage of this three-step process is ring opening of the epoxy groups with acidic water, a triol (trimethylolethane) or a tetrol (pentaerythritol) to give a polymer with a functionality of 2, 3 or 4, respectively. Finally, azidation of these polymers yields GAP polymers with higher functionality and reactivity.
Functionalisation of GAP with various other groups, is also possible. Frankel *et al.* [10] has patented a process whereby linear GAP is terminated with isocyanate groups to give an α,ω–diisocyanate functionalised GAP with the general formula:



$$OCN(CH_2)_6-NH-\overset{\overset{O}{\|}}{C}-\left[OCH(CH_2N_3)-CH_2\right]_n-O-\overset{\overset{O}{\|}}{C}-NH-(CH_2)_6NCO$$

α,ω–Diisocyanate GAP

and which was prepared by the reaction of GAP with hexamethylene diisocyanate. Alternatively, only one end of the chain can be functionalised with isocyanate and the other end with trimethylene propane, to give a trifunctional GAP isocyanate:



α–Isocyanate GAP

2.1.1 GAP Properties

The physico-chemical properties of GAP depend on the degree of polymerization, structure and method of preparation, see Table 1.

Table 1: GAP Diol and Triol Polymers [11]

	GAP Diol	**GAP Triol**
Density, g/cm^3	1.29	1.29
Colour	Lt. yellow liquid	Lt. yellow liquid
Heat of Formation, ΔH_f, cal/g	280	280
M_n	1700±300	≥900
Functionality	2.0	2.5–3.0
Vacuum stability, mL/g, 200 h, 100 °C	≥3	≥3
Tg, °C	–45	–45

GAP has a low glass transition temperature (–45°C) and a low weight percentage of polymer weight-bearing chain, which results in an energetically favourable binder system [12]. However at low temperatures GAP is hard and brittle as a consequence of the rigid, conjugated $-N_3$ groups limiting the flexibility of the polymer backbone. Further, the functionality of linear GAP is close to 2, and must be raised by the addition of triol or crosslinked with triisocyanate to generate the desired extended polymeric matrix. Gas evolution on curing the liquid GAP with isocyanates is also a serious problem. Isocyanates react with moisture to generate carbon dioxide, which remains trapped in the voids of the crosslinked binder and results in decreased mechanical properties, performance and safety of the explosive composition. Certain organometallic catalysts such as triphenyl bismuth, TPB and dibutyltin dilaurate have been found to suppress carbon dioxide formation, as well as promoting cure [13].
Gas generation can be readily expressed as:

$$R{-}N{=}C{=}O \quad + \quad H_2O \longrightarrow RNH_2 \quad + \quad CO_2\,(g)$$

$$R{-}N{=}C{=}O \quad + \quad RNH_2 \longrightarrow \underset{\textbf{urea}}{RNH\text{-}CO\text{-}NH\text{-}R}$$

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 [14]. GAP also contains a relatively high concentration of carbon atoms, and therefore has a high "combustion potential" [15], burning smoothly at elevated temperatures and pressure (>0.3 MPa) without explosion [16].

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. Kubota [15] has suggested that initial decomposition of GAP follows the reaction:

$$R{-}CH_2{-}N{=}N_2 \longrightarrow R{-}C{\equiv}N + N_2 + H_2$$

corresponding to the release of 685 kJ/mole, and that subsequent decomposition of the resulting nitrile leads to carbonaceous by-products. Differential scanning calorimetry (DSC) studies on GAP have been carried out by Leu *et al.* [17], who observed initial decomposition at 240°C, followed by degradation at 260-500°C.

GAP has a Hazard Classification of 1.3 (mass fire hazard), determined by standard explosive classification tests including initiation, unconfined burning, impact sensitivity and thermal stability. Results are shown in Table 2. GAP contributes an intrinsic energy content of 2500 kJ kg^{-1} [$\Delta H_{expl.}$ (calc.)] [3].

Table 2: GAP Explosive Classification Test Results [5]

Test	Result
#8 Blasting cap	
– Liquid	Did not detonate
– Cotton soaked liquid	Did not detonate
Unconfined burning	Burns smoothly and rapidly
Impact sensitivity	200 kg-cm
Thermal stability	0.5% wt loss after 8 days at 73.9°C

Sayles [18] and Dhar [19] both found that GAP reduces the impact sensitivity of AP/RDX based composite propellants.

2.1.2 Branched GAP

Branched GAP consists of a long GAP backbone chain, to which shorter GAP chains have been grafted. It is synthesised by the simultaneous degradation and azidation of high molecular weight solid polyepichlorohydrin (PECH) with sodium azide in the presence of a basic cleaving agent and polyol in a polar solvent (dimethyl sulfoxide, dimethylformamide or dimethylacetamide) [20].

The preparation of branched GAP with molecular weight ranges of 1000 to 2.0 × 10^5 by the degradation process was devised at DREV by Ahad [21]. Ahad prepared branched hydroxyl-terminated GAP polymers via the reaction of a high molecular weight polyepichlorohydrin (0.5 to 5.0 × 10^6) with an alkali metal azide in organic solvent with catalyst. Adjusting the catalyst/polymer weight ratio controls the molecular weight. Typical degradation catalysts include lithium methanolate and sodium hydroxide. Solvents used in this process must solvate the high molecular weight polymer as well as the sodium azide and catalyst in order to accomplish the combined degradation and azidation step effectively.

The result of this innovative degradation process is that it is now possible to obtain branched hydroxyl-terminated polymers in a single step, with subsequent reductions in time, cost and hazardous operations. A pilot-plant for the manufacture of 5 kg/batch branched GAP has now been commisioned at DREV [22, 23].

Some typical properties of branched GAP prepared by the degradation process are listed in Table 3. The molecular weights all decrease with a corresponding reduction in the functionality of the polymer. All the samples possess narrow molecular weight distributions and low glass transition points.

Table 3: Branched GAP Properties [24]

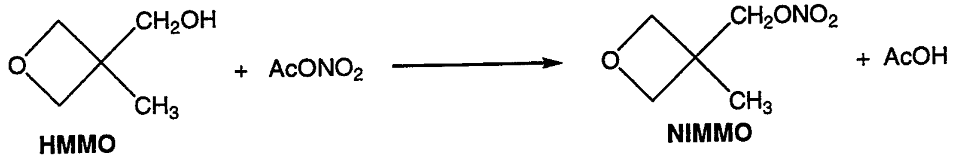
M_w	M_n	M_w/M_n	Functionality[a]	T_g (°C)	η, 25°C (cp)	ΔH_c (cal/g)
90 000	36 000	2.5	9.5	–45	500 000	–
22 000	10 000	2.2	3.7	–50	70 000	–4995
9000	4300	2.1	2.6	–50	39 000	–5025
5600	2800	2.0	2.4	–50	28 000	–5000
4400	2300	1.9	2.3	–55	22 000	–5010
3600	2000	1.8	2.3	–55	19 000	–
3200	1900	1.7	2.2	–55	16 000	–

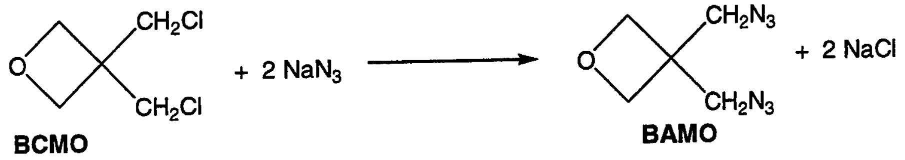
[a] Hydroxyl functionality determined by gellation technique [25].

The large hydroxyl functionality of the higher molecular weight polymers is an indication that GAP obtained by the degradation process contains branches possessing terminal OH groups. The degradation process allows for the synthesis of branched GAP with a lower Tg than its corresponding linear analog (Tg = –55°C for branched GAP and –45°C for linear GAP).

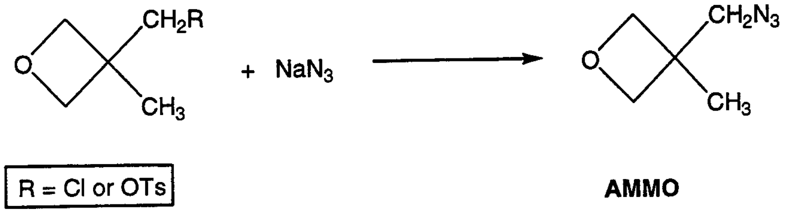
2.2 Oxetane Polymers

Energetic polyoxetanes were first synthesised by Manser from monomers such as 3-nitratomethyl-3-methyl oxetane (NMMO or NIMMO), 3,3-bis-(azidomethyl)oxetane (BAMO) and 3-azidomethyl-3-methyl oxetane (AMMO) [26]. NIMMO is prepared by the acetyl nitrate nitration of 3-hydroxy-methyl-3-methyloxetane (HMMO). The synthesis of BAMO involves treating 3,3-bis(chloromethyl)oxetane (BCMO) with sodium azide in dimethylformamide at 85°C for 24h.





AMMO, the mono-functional analog of BAMO, is synthesised by azidation with sodium azide of the chloro [27] or tosylate [28] product of 3-hydroxy-methyl-3-methyloxetane, HMMO.



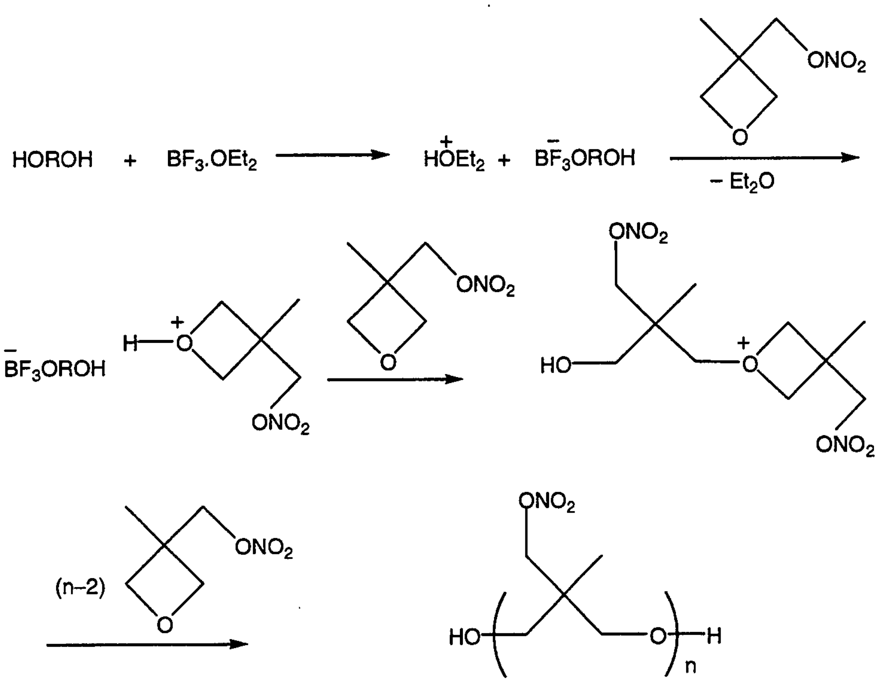
A more convenient synthesis of NIMMO can also be carried out using an alternative nitrating agent, dinitrogen pentoxide (N_2O_5) in a flow nitration system [29]. This nitration process gives excellent yields and produces sufficiently pure NIMMO that requires no further purification [30].

NIMMO is a low Tg monomer ideal in many munitions applications, BAMO is a solid symmetric monomer (m.p. ~80°C) 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.

2.2.1 PolyNIMMO

Traditionally, the polymerization of oxetanes to polyethers is achieved by cationic polymerization employing initiators (commonly diols) and catalyst (Lewis acid) [31],[32]. The mechanism of polymerizing NIMMO with boron trifluoride etherate catalysts is shown below and gives pale yellow liquid elastomers.



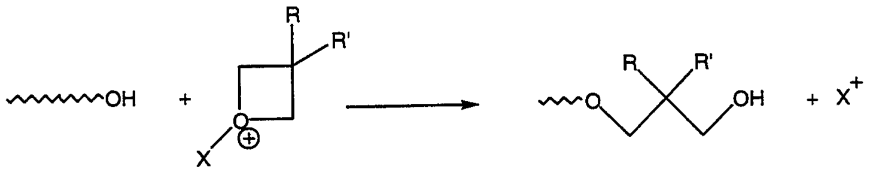
PolyNIMMO

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

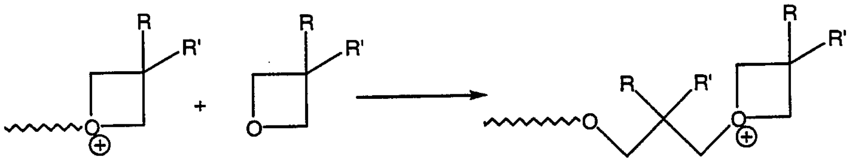
The polyNIMMO prepared above is difunctional, i.e. each molecule contains two hydroxyl groups, since 1,4-butanediol is the initiating alcohol ($R = -(CH_2)_4-$). The molecular weight can be adjusted by changing monomer feed rates and the ratio of diol to Lewis acid co-initiator. Generally, polymeric chains that terminate at both ends with primary hydroxyl groups possess an advantage over secondary or tertiary alcohols in that primary hydroxyl groups are more reactive towards isocyanate groups during cure. However, such primary hydroxyl reactivity can have an adverse effect in regards to the final cure stability of energetic binders. End-modification of the primary hydroxyl groups must be carried out to ensure a stable energetic binder with respect to its vacuum stability, aging and decomposition behaviour. For chain elongation, at least one isocyanate equivalent must be used; for crosslinking purposes, an isocyanate of higher functionality, or a separate crosslinking agent such as trimethylolethane or trimethylolpropane must be used.

The classical cationic polymerization of oxetanes described above suffers from several shortcomings, including a lack of molecular weight control and product reproducibility, poor initiator incorporation and the failure to adequately form copolymers of the desired structure [33]. Use of an activated monomer polymerization method changes the underlying mechanism from a cationic polymerization process to the attack of a hydroxyl-terminated polymer on an activated monomer as follows:

Activated Monomer Polymerization



Classical Cationic Polymerization



The salient feature of activated monomer polymerization is attack of an alcohol on an activated oxetane monomer, thus ensuring rapid and complete initiator incorporation into the polymer chain [34]. This method has several advantages over the classical cationic polymerization of oxetanes, primarily in avoiding the formation of unstable and highly active cationic propagating species.

The activated monomer polymerization yields copolymers with good molecular weight control and reproducibility, requires only catalytic quantities of a stable acid catalyst with an inexpensive alcohol initiator and is carried out at ambient temperatures. This is in complete contrast to the classical cationic polymerization route, which comprises a marginally stable co-initiator (typically BF_3 or $AgSbF_6$) with biscumyl chloride (BCC) co-catalyst and is carried out at –90°C. Catalysts employed for activated monomer polymerization range from boron trifluoride etherate, triethoxonium tetrafluoroborate, fluoroboric acid [35] to the spirosiloxane developed by Sogah [36].

2.2.2 PolyNIMMO Properties

Oxetane based polymers, such as polyNIMMO, offer low glass transition temperatures and miscibility with similar plasticisers, and are cured with conventional isocyanates upon heating. PolyNIMMO has an intrinsic energy content of 818 kJ kg^{-1} [ΔH_{expl} (calc.)] [3] and is classified as a non-explosive (UK classification).

Table 4 highlights relevant properties of commercial polyNIMMO, both difunctional and trifunctional species.

Table 4: Properties of Difunctional and Trifunctional PolyNIMMO [37]

Properties	**PolyNIMMO Difunctional**	**PolyNIMMO Trifunctional**
M_w[a]	17 000	6500
M_n[b]	12 500	4200
M_w/M_n[c]	1.36	1.55
Functionality[d]	≤2	≤3
Tg (DSC)	–30°C	–35°C
Onset of decomp. (DSC @ 5°C/min)	187°C	184°C
Stability (Vacuum Stability Test)	Very stable	Very stable
Impact Sensitivity (Rotter Test)	Insensitive	Insensitive
Viscosity, 30°C	1600	–
Purity	99%+	99%+
Recommended Cure Reagent	Desmodur N-100[e]	MDI

[a] M_w is the weight average molecular weight
[b] M_n is the number average molecular weight
[c] M_w/M_n is the molecular weight distribution.
[d] as determined by ^1H NMR
[e] commercial product (Bayer).

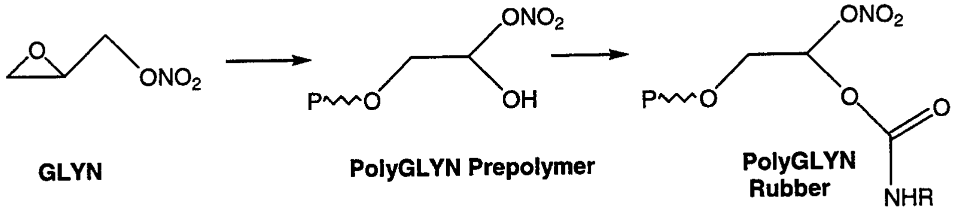
Aging and degradation studies on polyNIMMO have been carried out at DERA in the UK and showed that polyNIMMO exhibits gassing, although this can be reduced by the inclusion of stabilisers such as diphenylamine and 2-nitrophenylamine (1% wt/wt). Kinetic data obtained on polyNIMMO decomposition follows first order rate laws with no autocatalysis observed. The activation energy is in the range associated with the decomposition by nitrate ester bond cleavage [38]. The basic degradation mechanism involves homolytic scission of the $CH_2–O–NO_2$ bond to give $CH_2O•$ radicals and $NO_2•$ [39]. At temperatures greater than 120°C, the initial process is rapid and anaerobic, yielding both chain scission and crosslinking; at temperatures of around 60°C the reaction is slower, with atmospheric oxygen playing a greater part. Production of the $CH_2O•$ radicals and $NO_2•$ initiates auto-oxidation reactions involving peroxide formation, alkoxy and alkyl reactions, and reaction with oxygen to give chain scission of the polyether backbone.

2.3 Oxirane Polymers

Oxirane polymers possess similar physical and chemical properties to oxetane polymers, with the major difference being one fewer methylene group in the repeating unit.

2.3.1 PolyGLYN

Glycidyl nitrate (GLYN) is prepared by the nitration of glycidol, and is polymerised to give a hydroxyl terminated prepolymer. Urethane crosslinking with isocyanates leads to polyGLYN cured rubbers. However some confusion results from the term 'polyGLYN' being used for both the prepolymer and the cured rubber.



GLYN, like its oxetane counterpart NIMMO, is now prepared using N_2O_5 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 polyNIMMO) combined with a di-functional alcohol (glycol), to give a nominally di-functional polymer [40]. 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.

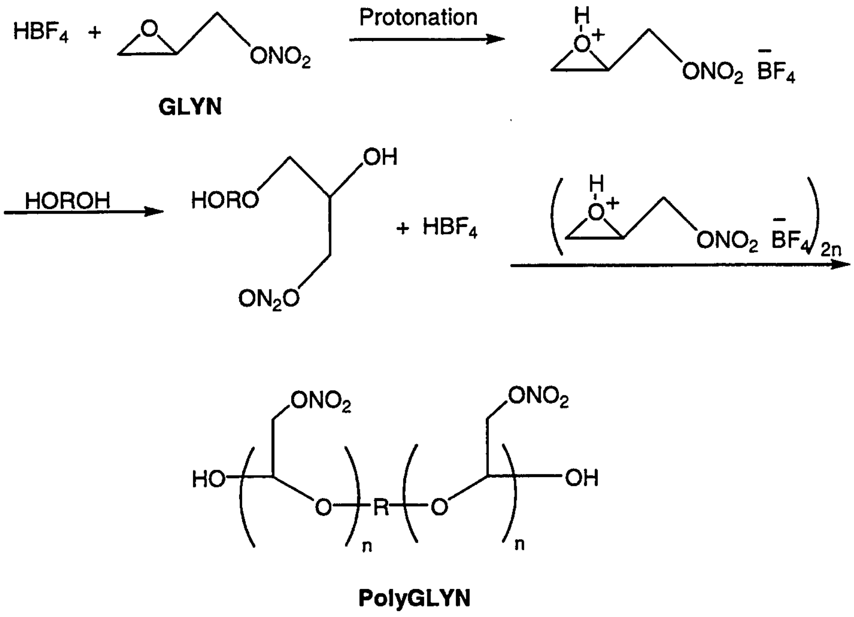


Figure 2: Active Monomer Polymerization of GLYN

2.3.2 Properties of PolyGLYN Prepolymer

PolyGLYN prepolymer is a clear, yellow liquid high in energy and density with a low Tg [Table 5]. In addition, its sensitiveness is classed as too low to require classification as a Class 1 explosive (UK classification). PolyGLYN has a calculated energy of 2661 kJ kg^{-1} [ΔHexpl. (calc.)], comparatively higher than both GAP and polyNIMMO (2500 and 818 kJ kg^{-1}, respectively) [3].

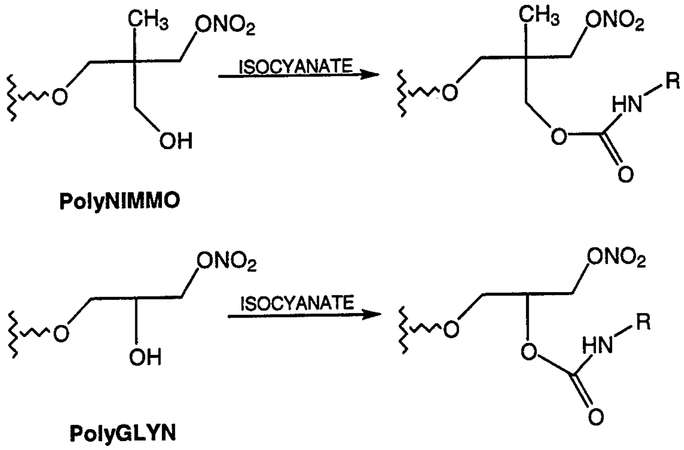
Table 5: Typical Properties of Poly(GLYN) [41]

PolyGLYN	
Density, g/cm^3	1.46
Tg, °C	–35
Heat of formation, kcal/mol	–68
Functionality	~2
Hydroxy value (mg KOH/g)	~37
O_2 balance	–60.5
Temp. of I, °C	170

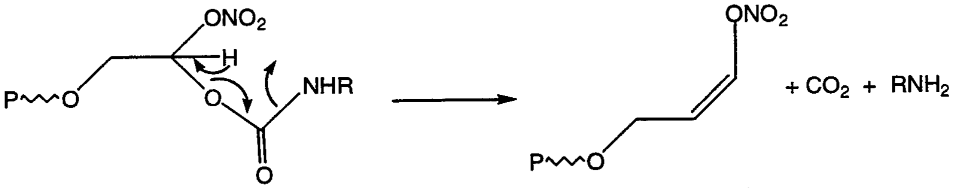
2.3.3 Stability of PolyGLYN Rubber

Uncured polyGLYN prepolymer exhibits good chemical stability. However, when cured with isocyanates the resulting polyurethane rubbers show poor stability. Long term or accelerated aging results in degradation of the rubber. Such dramatic aging was not observed in polyNIMMO rubbers (Fig. 3) [1].

Figure 3: Uncured and Cured PolyNIMMO and PolyGLYN



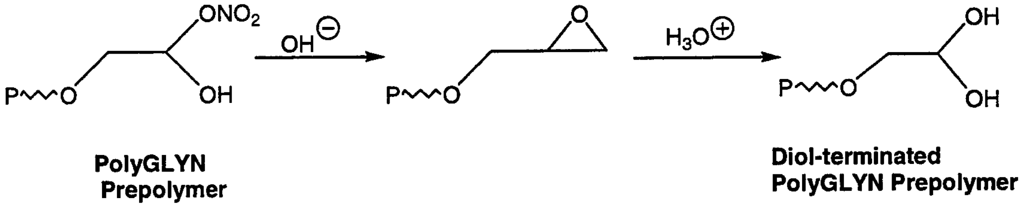
Further, degradation is not prevented by the presence of stabilisers, or by the exclusion of oxygen. This decomposition of polyGLYN rubber is attributed to a low activation energy degradation associated with chain scission at the urethane linkage and has little to do with the normal nitrate ester degradation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



PolyGLYN

This instability appears to be an inherent problem with polyGLYN prepolymer, and is not dependent on the isocyanate used. The problem has been overcome by modification of the chain ends to give a diol terminated polyGLYN prepolymer. Accelerating aging tests at 60°C in a sealed tube, and Shore Hardness measurements on polyGLYN cured with Desmodur N100 and isophorone diisocyanate (IPDI) reveals that the cured rubbers from unmodified polyGLYN degrade rapidly, while the sulphuric acid/THF end-modified rubbers maintain their structural integrity with good resistance to tearing.

Researchers then discovered that these end-modified polymers were exhibiting high gasssing rates. [42]. Vacuum stability tests showed that sulphuric acid/THF end-modified rubber had stabilities of around 2mL/g.[1] This problem has now been solved by effectively washing the diol terminated polyGLYN prepolymer. Modifications involve a 50% K_2CO_3 wash, followed by a 10% K_2CO_3 wash, and a THF/H_2O wash prior to isocyanate curing.



End Modification Route for PolyGLYN

2.4 Miscellaneous Nitrogenous Polymers

Miscellaneous nitrogen-containing polymers that have found use as energetic binders include polyvinylnitrate, polynitrophenylene, nitramine polyethers and *N,N'*-bonded epoxy binders. Recently the inert poly(furfuryl glycidyl ether) has also been identified as a possible route to energetic binders [43]. It is expected that energetic polymers can be produced via incorporation of explosophoric groups onto the poly(furfuryl glycidyl ether) backbone.

2.4.1 Polyvinylnitrate, PVN

Polyvinylnitrate, $-[CH_2-CH(ONO_2)-]_n-$, was devised to replace nitrocellulose binders, and was first synthesised in 1929 [2] by nitration of polyvinyl alcohol with mixed acids, [44] nitric acid in ether, [45] or nitric acid in chlorinated solvents [46]. The polymer has a density of 1.5 g/cm^3 and molecular weight over 100 000. Pure PVN has been found by vacuum stability tests to be more stable than nitrocellulose and has been added to cast-cured, double-base composite propellants to improve mechanical properties.

2.4.2 Polynitrophenylene, PNP

PNP is a thermostable, amorphous polymer of relatively low molecular weight (~2000) and is manufactured by Dynamit Nobel [47]. The polymer is obtained by Ullmann's reaction of 1,3-dichloro-2,4,6-trinitrobenzene with copper powder catalyst in

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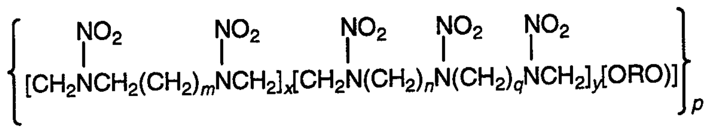
[1] The vacuum stability test measures the volume of gas evolved from a sample while it is heated at 100°C for 40 hours and is qouted in mL per grams. For comparison, the energetic binder polyNIMMO has a vacuum stability of around 0.5 mL/g [1].

nitrobenzene at 150°C. The polymer does not melt and is coated onto fillers by an acetone-ethanol solution and finds uses as a heat resistant binder for propellants.

2.4.3 Nitramine Polyethers

A recent patent [48] detailed the synthesis of nitramine functionalised polyethers by a solvent free, melt polymerization reaction process to yield polymers with low Tg, low viscosity properties and resistance to hydrolysis. The reaction of nitramine-containing monomer with a diol in the absence of solvent gives polymers of the type:



$$\left\{ [CH_2\overset{NO_2}{N}CH_2(CH_2)_m\overset{NO_2}{N}CH_2]_x[CH_2\overset{NO_2}{N}(CH_2)_n\overset{NO_2}{N}(CH_2)_q\overset{NO_2}{N}CH_2]_y[ORO)] \right\}_p$$

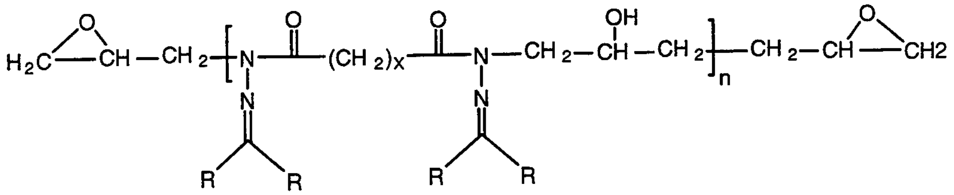
where R = $-CH_2CH_2OCH_2CH_2-$.

These polymers show high specific impulse in propellant formulations, a functionality close to 2, and a relatively low Tg (–18°C). They can be prepared in a molecular weight range from 500 to 10 000 by simply varying the stoichiometry of the diol and monomer.

2.4.4 *N,N′*-Bonded Epoxy Binders

These compounds are based on α,ω–epoxy functional compounds having *N,N′*-bonds in the backbone. Jain *et al.* [49],[50] has synthesised such compounds by the epoxidation of bis dicarbonylhydrazones of adipic, azelaic and sebacic dihydrazides (Fig. 4). They exhibit good propellant characteristics (superior ignition rates and increased burn rate) over conventional polybutadiene binders. Propellant samples were made by press-moulding together ammonium perchlorate (80%), *N,N′*-bonded epoxy binder (16%), diaminodiphenylmethane curing agent (4%) and dimethyl sebacate as plasticiser.

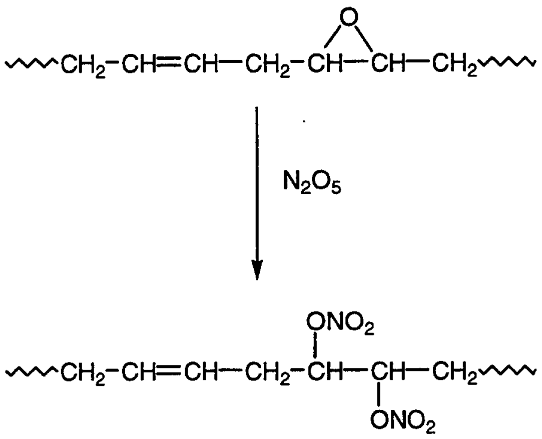
Figure 4: General Structure of N,N′-bonded Epoxy Binders



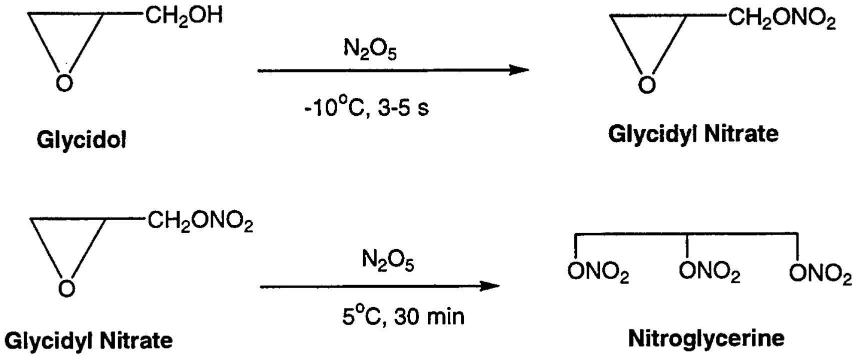
2.5 Nitration using Dinitrogen Pentoxide

The C-nitro ($C–NO_2$), nitramine ($N–NO_2$) and nitrate ester ($–ONO_2$) functional groups are basic building blocks for energetic materials, and are largely synthesised by nitration [51]. The classical nitration method using mixed acid (either 100% nitric acid or mixtures of nitric acid/sulphuric acid) is generally too severe for polyether backbones, and is not selective. However, reactions with dinitrogen pentoxide, N_2O_5 (produced by ozonation of N_2O_4, or by anodic electrolysis of N_2O_4 in 100% nitric acid) are quantitative and rapid, typically complete within minutes at ambient temperature. Furthermore, N_2O_5 has differing nitrating behaviour according to the medium in which it is employed. In 100% nitric acid there is a high degree of dissociation arising from the polarity of the solvent, leading to unselective nitration akin to that in mixed acids. However, nitrations carried out in organic solvents (preferably chlorinated hydrocarbons) involve undissociated N_2O_5 [52].

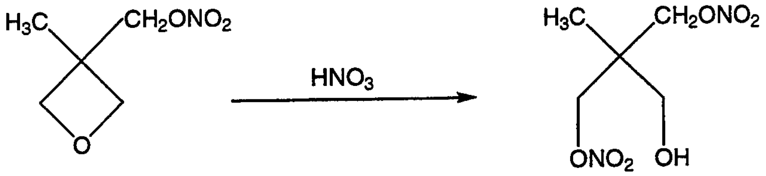
A further feature of N_2O_5 nitrations is that reactive polymer backbones can be nitrated without chain scission of the backbone. This feature can be observed in the partial nitration of polybutadiene in which only a portion of the double bonds have been converted to epoxy groups. If an equimolar amount of N_2O_5 is used to nitrate the epoxy groups, then ring cleavage is the only reaction observed, without attack at the olefin sites.



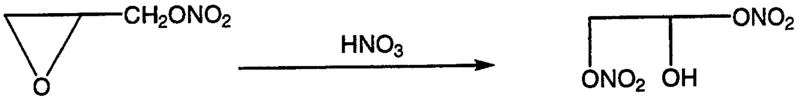
When preparing energetic binders by nitration with N_2O_5, care must be observed with regards to the temperature and time of reaction. For example, nitration of polyNIMMO and polyGLYN takes place at low temperature and within a few seconds, whereas nitration reactions of over 30 mins and with excess N_2O_5 produces ring-opening, as shown in the following GLYN example:



Monomer purity is vital for the polymerization step and care must also be taken to control reaction conditions to minimise ring-opening nitration. In addition, nitration of the hydroxyl group produces nitric acid which may also cause ring-opening to give a nitrate and another hydroxyl group [52].



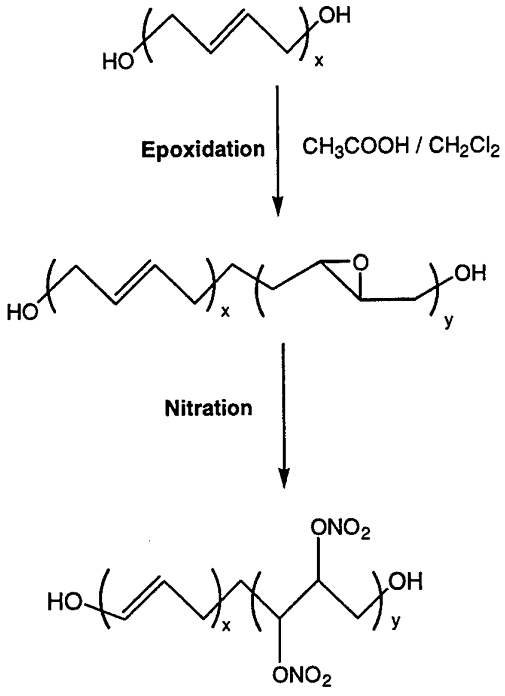
Oxetane



Oxirane

The nitration of the hydroxyl group is exothermic, and long addition times are required to control the exotherm. This problem has been overcome by nitrating in a continuous flow reactor followed by quenching with aqueous sodium carbonate solution [52].

The nitration of HTPB has been carried out by two reaction pathways; the classical route which employs a nitromercuration-demercuration route, or alternatively, epoxidising hydroxy-terminated polybutadiene and then nitrating with dinitrogen pentoxide [53], shown on opposite page.



NHTPB

It has been observed that the level of nitration in the final polymer affects the thermal stability and mechanical properties. Thus a level of nitration corresponding to 10% nitration on the polymer backbone will give a good compromise between energy output, mechanical properties and miscibility with energetic plasticisers. At this low level of nitration (10–15%) the glass transition temperature is kept low (<–50°C) with complete miscibility in most energetic plasticisers.

NHTPB has low viscosity, low Tg and is readily cured by isocyanates. Some typical properties of nitrated hydroxy-terminated polybutadiene at 10% nitration levels are given in Table 6.

Table 6: Properties of NHTPB [37]

M_w	8000
M_n	3000
M_w/M_n	2.66
Tg (DSC), °C	–58
Onset of decomposition (DSC @ 5°C/min), °C	150
Stability (Vacuum Stability Test)	Fairly stable
Impact Sensitivity (Rotter Test)	Out of range
Viscosity @ 30°C, poise	128

2.6 Fluorinated Polymers

Fluorinated polymers offer intrinsic advantages over inert hydrocarbons such as HTPB. Fluorocarbons have higher densities which results in formulations with higher densities and inherently higher performance. 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 hydroxy-terminated polymers. A general reaction scheme for the production of polyformals is shown below [54].

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

Various chain lengths have been prepared to give polymers with low Tg and find use as copolymers with other low Tg monomers.

In an US Patent, Adolph [55] describes an energetic binder comprising:

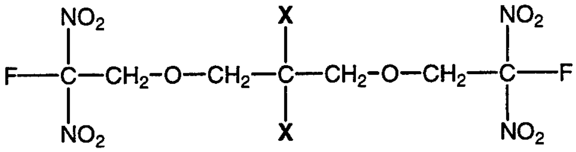
$$HO{-}CH_2(CF_2)_nCH_2[OCH_2OCH_2(CF_2)_nCH_2]_m{-}OH$$

which is a hydroxy terminated polyfluoroformal prepolymer with molecular weight between 1,000 and 10,000, and a compatible energetic plasticiser such as bis(2-fluoro-2,2-dinitroethyl)formal. The increased compatibility of the prepolymer with fluorinated plasticisers 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.

The novelty of this patent lies in the use of fluorinated polymers/plasticisers to form HMX-containing PBXs of the same energy (detonation pressure) as conventional nitrated polymers/plasticisers 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 [56]. 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 [57]. Furthermore, diflouroamine groups are relatively sensitive to impact.

The application of these functional groupings is illustrated in the structurally related SYEP and FDNA molecules, both prepared by Fluorochem [58],[59].



$$F{-}\underset{NO_2}{\overset{NO_2}{C}}{-}CH_2{-}O{-}CH_2{-}\underset{X}{\overset{X}{C}}{-}CH_2{-}O{-}CH_2{-}\underset{NO_2}{\overset{NO_2}{C}}{-}F$$

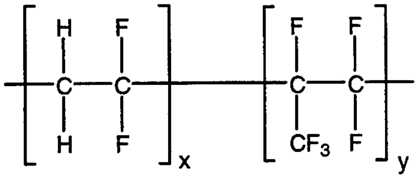
	SYEP ($X = NF_2$)	FDNA ($X = NO_2$)
Density, g/cm^3	1.691	1.640
Melting point, °C	–2.5	21
Specific Impulse, s	264.9	254.5
Detonation Pressure, kbar	273.75	249.05
Impact Sensitivity, cm/2.5 kg	141	158

Typically, SYEP has a lower melting point and a slightly lower oxygen balance than FDNA, but has a slightly increased density and enhanced specific impulse and detonation pressure. The measured impact sensitivity of SYEP is slightly higher, although caution must be exercised in any comparison of liquids with solids.

Recent advances made in the synthesis of dense, cyclic energetic materials can also be applied to polymers. The introduction of bis-(difluoramine) groups onto polymer backbones can now be made possible by the reaction of carbonyl compounds with difluoroamine in fuming sulphuric acid (difluorosulphamic acid) [60]. Difluoramine is generated in-situ by acid hydrolysis of *N,N*-difluorourea, which is prepared by direct fluorination of aqueous urea [61]. In this manner, fluorinated polymers can be synthesized readily and incorporated into PBX systems to boost energy output.

2.6.1 Fluorinated Copolymers

Copolymers of fluorinated polymers have found uses as inert binders with high densities for energetic compositions for the last 30 years. Copolymers are typically vinylidene fluoride and hexafluoropropylene, known commercially as Viton A (DuPont).



Copolymer of vinylidene fluoride/hexafluoropropylene

Such copolymers give high densities concomitant with high fluoride content and good thermal stability. In addition, fluorinated copolymers used in PBXs allow for processing methods such as ram extrusion and compression moulding without the loss of performance. A major disadvantage with these copolymers is the use of flammable solvents to process these copolymers with energetic ingredients. It is deemed an environmental and safety issue to remove such flammable solvents from energetic processing towards a solvent-free processing energetic system.

Adolph and Cason-Smith [62] have prepared randomly distributed copolymers of polynitrofluoroformals via the polycondensation of nitraminediols and fluorodiols with formaldehyde in sulpholane/boron trifluoride etherate solvent. Absence of side

reactions in the propagation and termination steps of the reaction results in polymers that are nearly 100% difunctional and terminated by fluorodiol monomer hydroxy groups (ideal for block copolymer synthesis and reproducible curing).
A general scheme for the production of polynitrofluoroformals is given by [63]:

$$\mathrm{RC(NO_2)_2CH(R')OH} \xrightarrow[\mathrm{H_2SO_4}]{\mathrm{CH_2O}} \mathrm{RC(NO_2)_2CH(R')OCH_2OCH(R')C(NO_2)_2R}$$

$R = F, NO_2, CH_3$; $R' = H$
or $R = F$; $R' = CH_3$

The crude copolyformal product contains unstable terminal hemiformal groups (–CH_2OCH_2OH) as well as labile dinitramine-derived terminal hydroxy groups. Removal of these groups to leave only the stable fluorodiol-terminated groups is accomplished by treating the mixture with hydrogen peroxide (30%).

$$\mathrm{RCH_2OCH_2OH} \xrightarrow{\mathrm{OH^-}} \mathrm{RCH_2OH} + \mathrm{CH_2O} \xrightarrow{\mathrm{H_2O_2}} \mathrm{HCOOH}$$

Recent advances in oxetane polymers have focussed on difluoramino oxetane copolymers, although the synthesis is rather cumbersome and costly at present [56]. Manser at Thiokol has found that copolymers comprised of difluoroamino and AMMO or BAMO monomers, have better thermal properties than the polymer (i.e. lower Tg), and this is believed to be due to the presence of the difluoroamine group [56]. The carbon atom connected to the difluoroamino group does not contain a hydrogen atom, which if present would cause the polymer to decompose to hydrofluoric acid, thereby reducing the thermal stability of the copolymer.

3. Energetic Plasticisers

The primary role of energetic plasticisers in energetic material formulations is to modify the mechanical properties of the charge 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 plasticiser can have secondary roles. 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 fulfil these roles, plasticisers 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

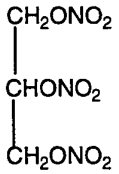
- absence of volatility and exudation (migration)
- low environmental impact
- availability and affordability.

By their own nature, plasticisers are typically oligomeric materials that have number average molecular weights ranging from 200 to 2000. Plasticisers 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 plasticisers between 400 to 1000 are considered to give optimum plasticising effect.

Like their polymeric counterparts, plasticisers can be inert (non-energetic) or energetic [64]. Non-energetic plasticisers are effective in improving mechanical properties, but degrade the output of the formulation by reduction of the overall oxygen balance. Examples of non-energetic plasticisers include the esters – acetyl triethyl citrate, diethyl adipate, diethyl sebacate and dioctyl adipate. Similar improvements in mechanical properties are desired from energetic plasticisers, but with a contribution to the oxygen balance and/or energy of the formulation. Energetic plasticisers 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 plasticiser 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 plasticiser.

3.1 Nitrate Ester Plasticisers

The first energetic plasticiser for commercial explosives – nitroglycerine (NG) or glycerol trinitrate – is a high performance nitrate ester having the following structure:

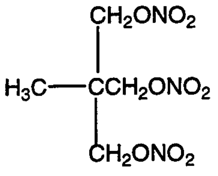


$$\begin{array}{l} CH_2ONO_2 \\ | \\ CHONO_2 \\ | \\ CH_2ONO_2 \end{array}$$

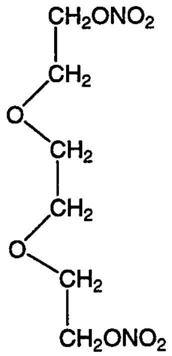
Nitroglycerine

First discovered in 1846, nitroglycerine is a sensitive explosive easily initiated by friction and impact. When heated above 200°C it will explode, while upon storage it proves unstable at temperatures exceeding 70-80°C [65]. In addition, NG exhibits significant physiological effects, causing dilation of the arteries and severe headaches. Nevertheless, nitroglycerine still remains an effective plasticiser for many applications.

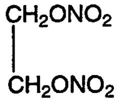
The nitrate esters have proved to be a fertile source of energetic plasticisers and a complete review is beyond the scope of this report. Some of the major nitrate esters in use today include trimethylol ethane trinitrate (MTN or TMETN), triethyleneglycol dinitrate (TEGDN), ethyleneglycol dinitrate (EGDN or nitroglycol), and butanetriol trinitrate (BTTN). Being structurally similar to NG, they were developed to replace this material; most of these molecules possess some of NG's properties without the severe hazards of NG.



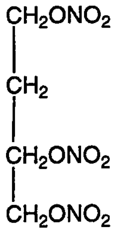
MTN or TMETN



TEGDN



EGDN



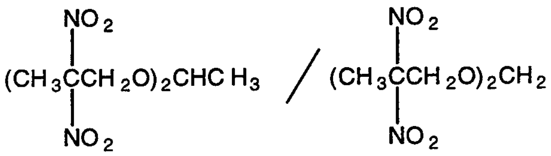
BTTN

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 plasticiser 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. It has a lower density than NG but offers improved stability.

Most of the energetic nitrate esters are HD 1.1 explosives that possess low critical diameters, high volatility and high sensitivity, making them difficult to handle.

3.2 BDNPA/F Plasticisers

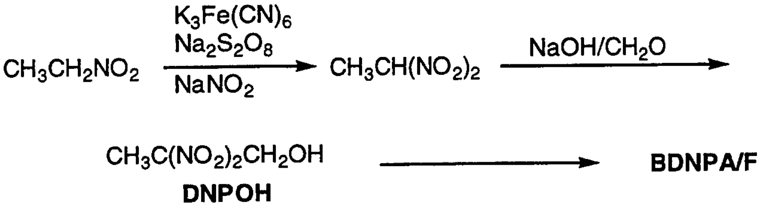
Plasticisers composed of bis(2,2-dinitropropyl)acetal (BDNPA) and bis(2,2-dinitropropyl)formal (BDNPF) have found widespread application in energetic formulations. For example, US Army applications such as the M900 tank program, LOVA gun propellant and the insensitive HMX-based explosive PAX-2A all use BDNPA/F as an energetic plasticiser. PBXN-106 used to fill the US Navy 5"54 gun also contains BDNPA/F [66].



$$(CH_3\overset{NO_2}{\underset{NO_2}{C}}CH_2O)_2CHCH_3 \;/\; (CH_3\overset{NO_2}{\underset{NO_2}{C}}CH_2O)_2CH_2$$

BDNPA/F

BDNPA/F plasticisers are typically 50/50 mixtures. The formal is a solid, slightly less energetic than the liquid acetal and is used to form an eutectic to lower the melting point (making plasticiser useable at lower temperatures) [67]. BDNPA/F was first developed by oxidative nitration of nitroethane to 2,2-dinitropropanol (DNPOH) with silver nitrate as catalyst [66]. This nitration process was uneconomical because of problems with waste and loss of silver (~1%) and was modified further to include a selective chlorination step of nitroethane to 1-chloronitroethane. By replacing chlorinated solvents with MTBE (methyl-*tert*-butyl ether), the process has now been made environmentally friendly. The nitration is also now carried out with inexpensive persulphate salts as the oxidant with a catalytic amount of potassium ferricyanide. Furthermore, the synthesis of BDNPA/F is now automated and run continuously to give high output of product [68].



$$CH_3CH_2NO_2 \xrightarrow[NaNO_2]{K_3Fe(CN)_6,\ Na_2S_2O_8} CH_3CH(NO_2)_2 \xrightarrow{NaOH/CH_2O}$$

$$\underset{\textbf{DNPOH}}{CH_3C(NO_2)_2CH_2OH} \longrightarrow \textbf{BDNPA/F}$$

BDNPA/F exhibits poor plasticising properties in terms of lowering Tg and viscosity of uncured PBX formulations. Furthermore, BDNPA/F may become unstable under severe conditions, such as a combination of elevated temperatures (>74°C) and high shock loading (#8 blasting cap with 33 g composition C-4 booster) [69].

3.3 Azido Plasticisers

The poor mechanical properties of azide functional polymers like GAP can be improved markedly by incorporation of energetic azido functional plasticisers. The synthesis of low molecular weight azido polymers such as GAP plasticisers can be achieved in a single process involving azide displacement of chlorine from epichlorohydrin monomer, ECH, followed by polymerisation without the need for a catalyst [70]. GAP plasticisers 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 plasticisers are given in Table 7 below.

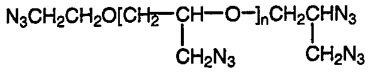
Table 7: Properties of GAP Plasticisers [11]

Properties	**GAP Diol**	**GAP Triol**
ΔH_f, cal/g	+280	
Density, g/cm^3	1.29	1.29
Colour	light yellow liquid	light yellow liquid
M_n	1700 ± 300	≥ 900
Functionality	2.0	2.5 – 3.0
Thermal Stability, 100°C (cm^3), 200h, mg/L	≥ 3	≥3
Tg, °C	– 45	– 45

As a general rule, plasticising effect will be lost if terminal hydroxyl groups on the plasticiser react with the isocyanate crosslinking agent, effectively tying the plasticiser into the cross linked polymer matrix. With this in mind, Ampleman [71] developed the synthesis of an azide terminated glycidyl azide plasticiser (GAPA), a plasticiser having no reactive terminal hydroxyl groups available for isocyanate cure. GAPA is a pale yellow liquid with low molecular weight, low Tg and good stability.

Table 8: Properties of Azido-Terminated GAP Plasticiser (GAPA) [11]

ΔH_f, cal/g	+ 550
Density, g/cm^3	1.27
Colour	light yellow
M_n	700 – 900
Thermal Stability 100°C (cm^3), 200h, mg/L	≤3
Tg, °C	– 56

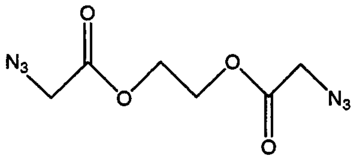


$N_3CH_2CH_2O[CH_2-\underset{CH_2N_3}{CH}-O-]_nCH_2\underset{CH_2N_3}{C}HN_3$

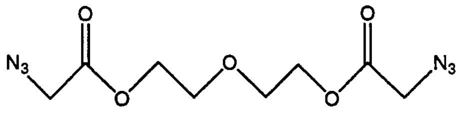
GAPA

3.3.1 Miscellaneous Azido Plasticisers

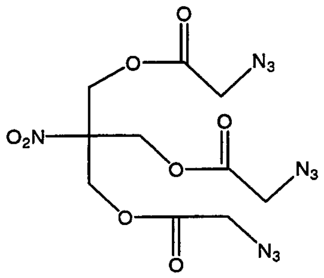
A new class of energetic plasticisers based on azido-acetate esters have recently been reported as giving binders with low Tg, good thermal stability and compatibility [72]. Four new compounds have been described, namely ethylene glycol bis(azidoacetate) (EGBAA), diethyleneglycol bis(azidoacetate) (DEGBAA), trimethylol nitromethane tris(azidoacetate) (TMNTA), pentaerythritol tetrakis (azidoacetate) (PETKAA). Properties are given in Table 9.



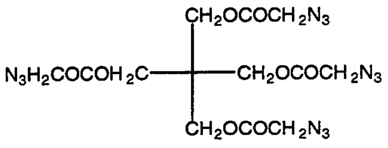
EGBAA



DEGBAA



TMNTA



PETKAA

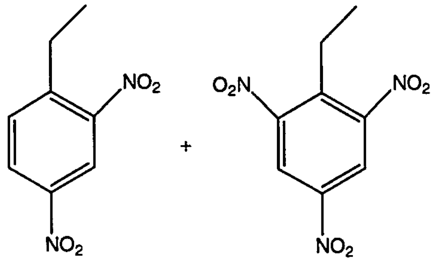
Table 9: Physical and Stability Properties of Azido Plasticisers [72]

Phys. Prop.	EGBAA	DEGBAA	TMNTA	PETKAA
Density, g/cm^3	1.34	1.00	1.45	1.39
O_2 balance, %	-84.15	-99.92	-71.95	88.82
ΔH_f, kJ/mol	-167.36	-328.86	-230.54	-215.2
Viscosity, mPas	23.4	29.2	1288	2880
Tg, °C	-70.8	-63.3	-34.1	-35.4
Stab. Props.				
Deflagration point, °C, (5K/min)	232	235	214	234
Weight loss, (90°C @ ca. 80 days, %)	0.9	0.48	0.25	-
Impact sensitivity, Nm	5.5	>10	16	60
Friction sensitivity, N	165	160	192	360

The new plasticiser (EGBAA) has been combined with polyNIMMO at 50% plasticiser loading to give a rubber with a Tg of -66.7°C with good stability [72].

3.4 K10 Plasticiser

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



K10

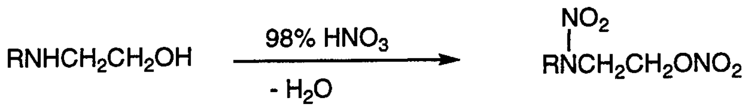
3.5 Nitrato Ethyl Nitramine Plasticisers (NENA)

The nitratoethylnitramine family (NENAs) are effective plasticisers in energetic formulations, particularly in nitrocellulosic systems. NENAs contain both nitrate ester and nitramine functionalities, and have the following structure:

$$RN(NO_2)CH_2CH_2ONO_2$$

Typical NENA derivatives in use include (R=) methyl, ethyl, propyl, iso-propyl, butyl, and pentyl (the structurally related 1,5-diazido-3-nitrazapentane, or DANPE, is often considered with the NENAs). The NENAs have been known since the 1940s, where DINA (dinitroxy ethyl nitramine) was scaled-up for use in Navy flashless gun propellants [73],[74]. It was not until the late 1970s where researchers at Eglin AFB used NENAs in gun propellants that required low flame temperatures and low molecular weight [75].

NENAs are readily manufactured by nitration of commercially available alkyl ethanolamines, in high yields (80%).



$$RNHCH_2CH_2OH \xrightarrow[-\,H_2O]{98\%\ HNO_3} R\overset{NO_2}{\overset{|}{N}}CH_2CH_2ONO_2$$

The use of NENAs as plasticisers in gun and rocket propellants confer excellent properties such as high burning rates, reductions in flame temperature and product gas molecular weight, and higher specific impulse (based on moderate loadings of 60-70% RDX in a nitrocellulose/NENA binder) [76].

NENAs possess good thermal stability, readily plasticise nitrocellulose and other polymers, generate low molecular weight combustion gases, and give good impact sensitivity [77],[75]. Important properties are listed in Table 10.

Table 10: NENA Properties [77]

	MeNENA	**EtNENA**	**PrNENA**	**BuNENA**	**PentylNENA**
Molecular Wt.	165.1	179.1	193.2	207.2	221.1
ρ, g/cm^3	1.53	1.32	1.264	1.211	1.178
m.p., °C	38-40	1-5	-2	-27 to -28	-8 to -5
O_2 balance	-43.6	-67.0	-87.0	-104.0	-119.1
DSC exotherm, °C	218	210	210	210	-
ΔH, kJ/mol	1113	784	503	259	47

One of the main disadvantages of NENAs as plasticisers is migration from compositions on standing or on long-term aging. While offering excellent initial plasticising effects, they are low molecular weight materials that are volatile and migrate readily from the polymeric binder system [77]. Consequently, propellant formulations containing NENAs have difficulty achieving 10-year service life [78].

On the other hand, recent research on polyNIMMO and polyGLYN binders has shown that BuNENA significantly decreases glass transition temperature *without* plasticiser migration [79]. Trifunctional polyNIMMO and BuNENA plasticiser in a 1:1 ratio gives a binder system having a Tg of –61°C. Campbell *et al.* [80] have shown that NENA plasticisers are better than BDNPA/F at reducing the viscosity and Tg of polyNIMMO cured rubbers.

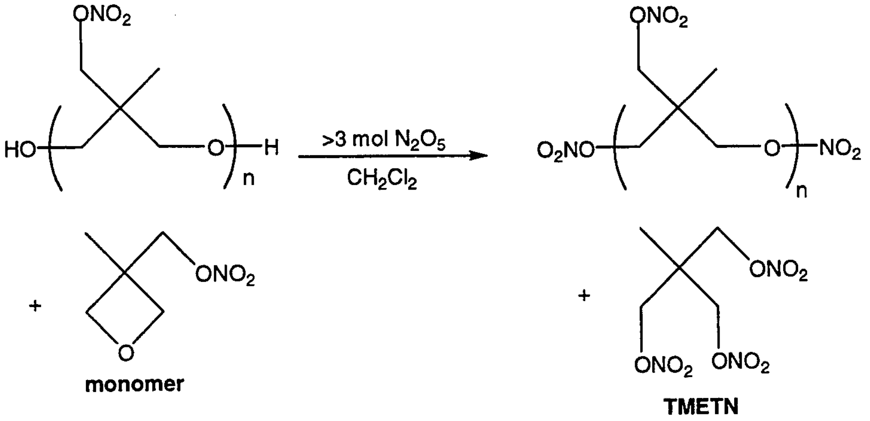
One disadvantage of NENA plasticisers is a potential incompatibility with ammonium perchlorate [81]. In the past such ammonium perchlorate and nitrate esters issues have been resolved by the inclusion of free radical scavengers (2-nitrodiphenylamine or alkaline additives such as sodium bicarbonate). Neither have proved as effective for NENAs. The authors suggest the use of alkyl ureas as effective stabilisers for NENAs when used in combination with AP [81].

3.6 Oxetane Plasticisers

Migration of the plasticiser 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 plasticisers that resemble even more closely the polymer matrix, enhancing physical and chemical compatibility and, hopefully, minimising migration. Melting point and glass transition temperature are clearly the most critical criteria, but other important considerations include energy balance, energy content and safety.

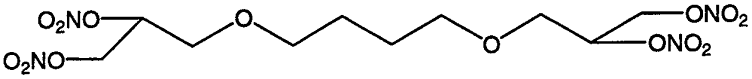
A cyclic tetramer of NIMMO was prepared at DERA. This compound, which is also present in commercial polyNIMMO (5-10%), has a relatively high Tg and is not an effective plasticiser. Linear NIMMO oligomers (polymers consisting of between 1-10 monomer units) were therefore prepared for use as plasticisers in polyNIMMO binder systems. Oligomeric NIMMO has a lower Tg than the cyclic tetramer but still contains NIMMO monomer.

In order to remove the terminal hydroxy groups, and prevent unwanted reaction with the isocyanate crosslinking agent, oligomeric NIMMO 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 NIMMO monomer into TMETN. Separation of the TMETN and isolation of purified nitrato oligomers is currently in progress at DERA [82].



3.7 GLYN Dimer Plasticiser

In a similar fashion, a derivative of glycidyl nitrate described as "GLYN dimer" has been prepared at DERA for plasticisation of polyether binder systems such as polyGLYN and polyNIMMO.



"GLYN Dimer"

The linear "GLYN dimer" molecule is significantly smaller than polyGLYN, and is prepared by end capping a 1,4-butanediol spacer unit with GLYN, and then nitrating the terminal hydroxy groups [83]. As with the NIMMO oligomer, nitration both increases oxygen balance and energy content, and prevents unwanted reaction of the plasticiser with the isocyanate crosslinking agent. "GLYN dimer" is normally a mixture of oligomers and has a low Tg (-64.9°C), and impact sensitivity compared with nitrate esters such as BTTN and TMETN. Some important properties are listed in Table 11.

Table 11: "GLYN Dimer" Properties [83]

Tg, °C	Density, g/cm^3	%H_{50}, cm	T of I, °C	VoD, m/s	P_{CJ}, GPa	ΔH_f, kcal/mol
-64.9	1.38	18.1	167	6900	17.7	-188.6

"GLYN dimer" also has a calculated explosive performance superior to K10, BuNENA and BDNPA/F. Initial studies of polyGLYN with "GLYN dimer" as plasticiser have produced well-cured binders with good mechanical properties. It is anticipated that the "GLYN dimer" will be less susceptible to migration than the more conventional plasticisers.

4. Conclusions and Recommendations

1. The use of energetic binder systems is a promising means of enhancing the output of cast cured polymer-bonded explosives and cast composite rocket propellants. This technology shows promise for use in high performance cast cured explosives for volume constrained and metal accelerating applications, and in advanced minimum smoke rocket propellants.
2. If energetic binders can be made to replicate the mechanical properties of inert binder systems such as those based on HTPB, then IM-compliant high performance explosives and propellants should be possible. Conversely, the use of energetic

binder systems may allow the performance of a composition to be maintained while the level of energetic (and sensitive) nitramine solid is reduced, offering an alternative approach to the formulation of IM-compliant energetic materials. It is therefore appropriate for DSTO to conduct research and development to explore this technology for future generations of energetic material compositions to address the evolving needs of the ADF.

3. While fluorocarbons find use as binders/desensitisers in pressed explosives, and azido-substituted polymers such as GAP, AMMO and BAMO are effective as the polymer matrix in rocket propellants, the most promising polymers for application in explosives are isocyanate-cured nitrato-substituted polyethers, where the nitrato group contributes to both the energy and the oxygen balance of the formulation. PolyGLYN is currently the most energetic polymer available, although the polyNIMMO technology is more mature.
4. Given the available level of effort, it is appropriate at this point in time for DSTO to conduct its research using commercially available ingredients, rather than developing its own. The US nitrato oxetanes are not currently available, while ICI Explosives is supplying research quantities of polyNIMMO and polyGLYN. The DSTO programme will therefore be based on these polymers.
5. Most effective use of energetic polymers will be achieved by inclusion of energetic plasticisers to modify the mechanical properties. The most promising energetic plasticisers for use with nitrato substituted polyethers appear to be the NIMMO oligomers and "GLYN dimer", although these materials are not yet fully charaterised, nor are they commercially available. The most practical short-term solution appears to be for DSTO to use the nitroaromatic plasticiser K10 manufactured by RO and employed by researchers at DERA.
6. The cost of polyNIMMO and polyGLYN is currently high, and immediate application is likely to be restricted to high performance cast-cured metal accelerating explosives. Likely candidates are high solids loading HMX-based PBX's, targeting Octol-like performance. Pragmatically, it may be sensible to conduct initial research on RDX analogues, aiming at cast-cured PBX's with the performance of Composition B.
7. Following initial characterisation of successful binder systems, DSTO research should address the explosive performance of PBX's composed of solid nitramines suspended in a matrix of energetic binder. The mechanical properties of these compositions and their response on generic IM-tests must then be investigated.

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19. ABSTRACT

In an effort to comply with Insensitive Munitions (IM) criteria, energetic binders comprising polymer and plasticiser(s) are finding use in cast-cured polymer bonded explosives and cast composite rocket propellants. Energetic binders can be considered as cross-linked polymers that provide a matrix to bind explosive ingredients together with a plasticiser. Once cured, the polymeric binder is a tough elastomeric rubber capable of absorbing and dissipating energy from hazardous stimuli, lending itself well to IM applications. This general document outlines the most promising energetic polymers and plasticisers being considered today.

Attention is focussed on several energetic polymers including glycidyl azide polymer, GAP, poly(3-nitratomethyl-3-methyloxetane), polyNIMMO and poly(glycidyl nitrate), polyGLYN, although several other energetic polymers will also be reviewed. Energetic plasticisers including oligomers (low molecular weight) of the polymers mentioned above, as well as a variety of nitrate esters, nitroaromatics and azido plasticisers, will also be reviewed. Finally, the review will recommend binder systems for DSTO's future energetic binder programs.