Ring-Opening Polymerization (ROP) for the Synthesis of Energetic Polymers (EPs)

A document prepared by Innovative Science, Inc. (Formerly Stewart's
Technologies, LLC)

for a Major Defense Contractor

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3154 State St.
STE 2300
Blacksburg, VA 24060
Voice: 540-998-9552
Fax: 540-961-6392
www.innovscience.com
slewis@innovscience.com

Executive Summary

Since the early 1980s, several approaches to ring-opening polymerization (ROP) of energetic monomers (EMs) have emerged. All operate by *cationic* mechanisms, which require chlorinated solvents and suffer from poor control over both molecular weight and polymer microstructure. The commercial scope and longevity of current ROP systems are therefore limited.

Innovative Science, Inc. (ISI) has developed *unique insight* into the fundamental flaws of current ROP methods. ISI is thereby poised to undertake *research*, on a contractual basis, that will lead to useful, potentially patentable improvements on current ROP methods. ISI also maintains a broad portfolio of intellectual property, including novel, commercially viable approaches to ROP that entirely circumvent the deficiencies of previously developed methods. ISI technologies offer the following features:

- Utilization of existing energetic monomers.
- Better control over polymer composition, molecular weight, and microstructure.
- Not limited to cationic processes.
- More environmentally friendly (i.e. green) conditions.

Section 1 of this document presents a brief review of current ROP methods, highlighting their key strengths and weaknesses. The aim of this review is to convince Major Defense Contractor (MDC) scientists and managers that ISI is prepared to address these weaknesses – and to advance entirely new ROP technologies – through a contract research arrangement with MDC. However, because non-disclosure agreements are not yet in place, the specific remedies and novel technologies offered by ISI must be reserved for future discussion. Section 2 describes a "Stage-Gate" approach that ISI has adopted to organize its research activities in a goal-oriented manner while maintaining objective merit criteria for continuation. The last section addresses contractual and IP issues, including deliverables (materials and reporting), patents, licensing, and royalties.

Forward

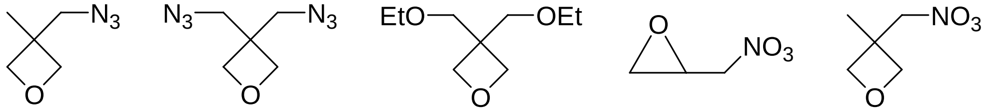
The information contained in this document is considered public knowledge and is intended to initiate a discussion between ISI and MDC that will hopefully lead to a mutually beneficial business relationship based on a contract research arrangement. As this relationship evolves, additional documents detailing ISI intellectual property can be made available to MDC. Although this initial document does not advance novel ideas, it does describe specific problems with existing ROP technologies. In some cases, even the *fundamental* reasons behind the *apparent* problems with current ROP methods – as well as the technical solutions to those problems – are not obvious, even to those skilled in this field and must therefore be withheld until non-disclosure agreements are in place. Even though some details are not presented here, the overall message is clear: ISI is prepared to develop new ROP technologies that offer better control over polymer structure and decreased environmental impact.

Section 1: Literature Review.

This section is not an exhaustive review of the vast literature on ROP. Rather, we highlight only the most important background information and recent developments in the field so that the strengths and limitations of present-day methods can be examined objectively. We show that despite intensive research in the field, step-change improvements are still possible, especially with regard to control over product composition and elimination of chlorinated solvents.

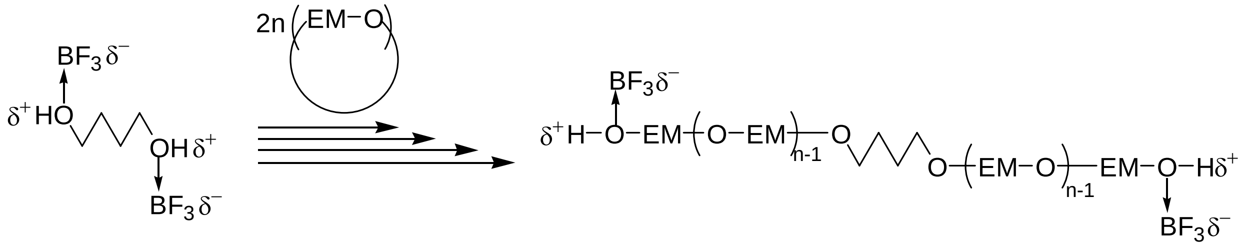
1.1 Protic Initiators

Cationic ROP is long-recognized as a useful method for the production of polyethers.[1] Manser and co-workers[2] extended this technique to energetic polymers. They focused on ROP of energetic cyclic ethers (Chart 1, Scheme 1), using an alcohol (proton source) and boron trifluoride etherate (activator) as the activator system – and dichloromethane as the solvent.



AMMO BAMO BEMO GN NMMO

Chart 1



EM = energetic monomer
System based on1,4-butanediol shown

Scheme 1

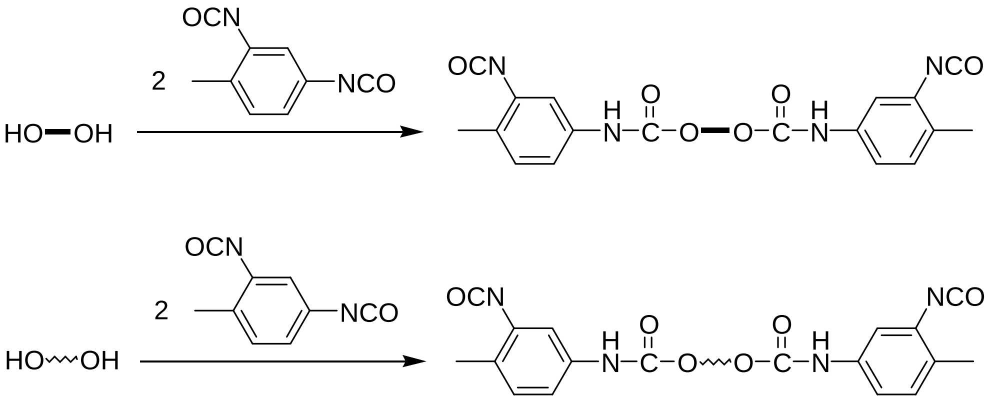
Based on surprisingly weak experimental data, Manser claimed that manipulation of the monomer to initiator ratio effected control of molecular weight.[2] Low molecular weight α,ω–dihydroxyl telechelic polyBAMOs with low polydispersity indices (PDIs) were produced,[2a] but on the other hand, the same polymerization technique afforded polyBEMOs with PDIs ranging from 6-16.[2d] This disparity was not convincingly explained, ISI knows the cause of this behavior (confidential information). Other drawbacks include the use of chlorinated solvents and large quantities of corrosive boron trifluoride to achieve useful products.

Other researchers[3,4] noted the ill-behaved nature of Manser's polymerizations and concluded quite reasonably that his system would not offer the necessary molecular weight control to be viable for commercial production of well-defined energetic thermoplastic elastomers (TPEs). However they also erroneously concluded that secondary initiation arising from adventitious moisture is the cause of this behavior. For instance, Sanderson[5] attempted to scavenge adventitious water using calcium hydride. Although he achieved improvements in productivity while suppressing cyclic oligomers, molecular weights were still well below theoretical values based on monomer-to-initiator ratios. Manser and co-workers also draw flawed conclusions on the structure-property relationship among initiator components. For example, they claim that 1,4-butanediol has reduced activity compared to other diols and requires larger amounts of boron trifluoride for efficient initiation.[2a]

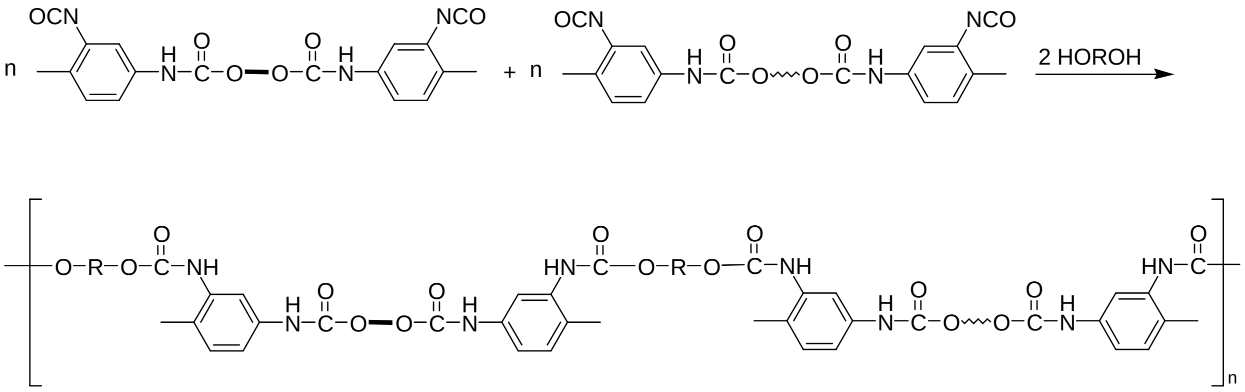
Manser and co-workers[2b,d] reported the synthesis of energetic TPEs produced by this polymerization system using two separate strategies. In the first strategy (Scheme 2), glassy and rubbery energetic α,ω–dihydroxyl telechelics were prepared (individually) and then linked together (in a stepwise manner) using phosgene or a diisocyanate. Sanderson and co-workers[5b-d]

Scheme 2

improved upon this approach by switching to an aromatic diisocyanate possessing isocyanate groups that exhibit vastly different reactivities (Scheme 3). The reactive group effected rapid end-group derivatization of the precursor α,ω–hydroxylic telechelics while the less reactive group impeded chain extension. Subsequently, rubbery and glassy α,ω–isocyanate telechelics are combined with a diol to furnish energetic TPEs (Scheme 4).



Scheme 3

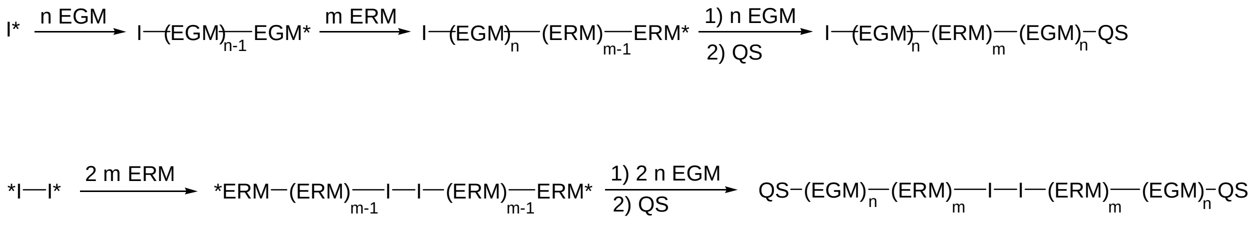


▬ = glassy block 〰 = rubbery block Ideal structure shown, polymer will be random

Scheme 4

Due to the random nature of these reactions, post-linking approaches cannot produce TPEs of discrete structure. Instead, a distribution of products will exist (i.e. diblocks). The presence of such materials have been shown to be detrimental to the physical properties of TPEs.[6] Moreover, agents of reduced toxicity would be desirable from an environmental standpoint. This strategy maybe disadvantageous as secondary bonding (i.e. hydrogen bonding) between linking groups may prevent such TPEs from performing well under adverse environmental conditions.

Manser's second approach to energetic TPEs involved sequential living block copolymerizations (Scheme 5). A monofunctional initiator requires three sequential monomer charges where the first and last charges form outer glassy blocks and the intermediate charge forms an inner rubbery block. A difunctional initiator requires only two sequential monomer charges to achieve a comparable overall structure. No physical data was provided for TPEs afforded by this route, and these polymerizations have been shown to be uncontrollable at times. The advantage of this method is that TPEs can be prepared in one-pot provided that control issues are properly addressed.



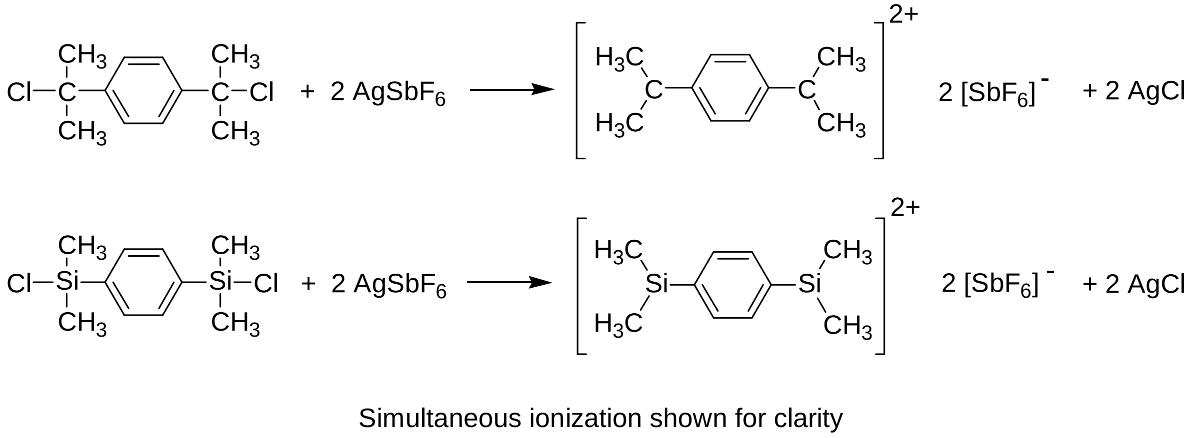
I* = initiating species; ERM = energetic rubbery monomer; EGM = energetic glassy monomer; QS = quenching species

Scheme 5

To comprehend the nature of the processes that lead to control issues with this type of initiator system one must be trained in the area of cationic polymerizations. Although such knowledge allows for identification of the causes for this behavior special insight in this field (i.e. that possessed by ISI) is required to solve these problems. The techniques advanced by ISI also offer reduced environmental impact.

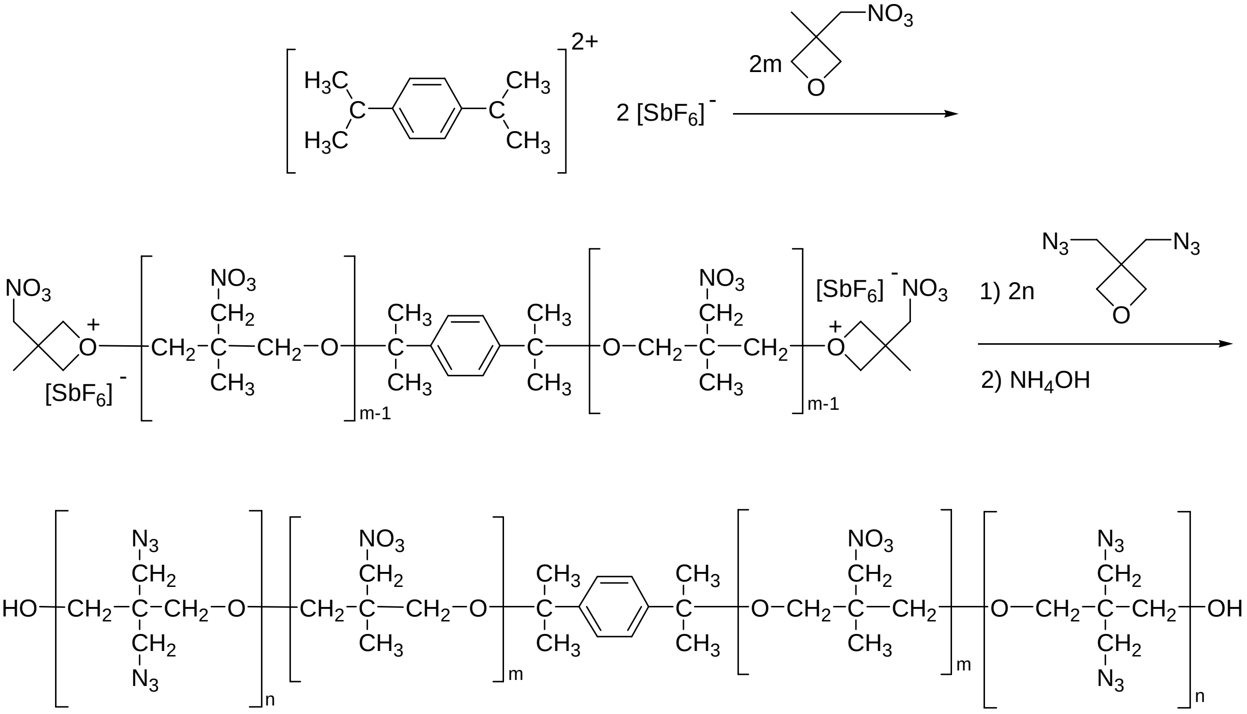
1.2 Carbocationic Initiators

Talukder and co-workers[3] used an alternative approach for ROP of energetic monomers that derived from a system originally developed by Kennedy and co-workers[7] for the polymerization of vinyl ethers. Initiating systems comprised a carbocation synthetic equivalent such dicumyl chloride (DiCumCl) or bis(chlorodimethylsilyl)benzene (BSB) in conjunction with the activator $AgSbF_6$ (Scheme 6). Polymerizations were carried out in dichloromethane solution at low temperatures (-78 °C).

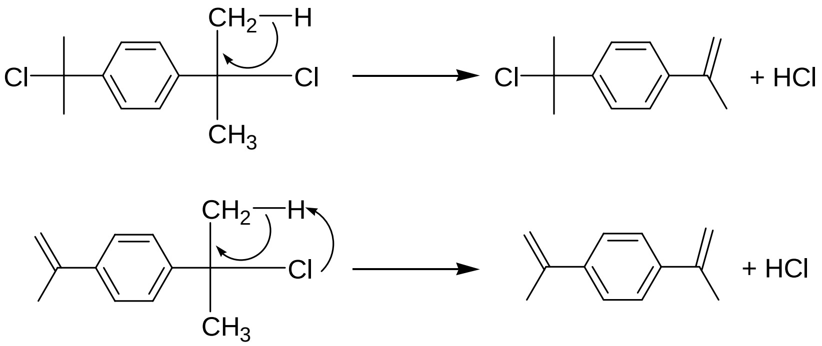


Scheme 6

Energetic TPEs were initially prepared by sequential block copolymerization of BAMO (hard segment) followed by NMMO (soft segment), initiated by $DiCumCl/AgSbF_6$ (Scheme 7). ^1H NMR and IR spectroscopic analyses confirmed the existence of BAMO and NMMO segments, while gel permeation chromatography-low angle laser light scattering (GPC-LALLS) showed that the PDIs of the TPEs were relatively low ($\overline{M}_w / \overline{M}_n = 1.2$). Talukder inferred quasi-living behavior. However, actual molecular weights exceeded the theoretical values (almost tenfold), suggesting that living-type control over $\overline{M}_n$ was not possible. The high $\overline{M}_n$ values were ascribed to thermal decomposition of DiCumCl (Scheme 8),[8] which would lower the number of active initiating species.[3b] However a follow-up experiment[3b] using AMMO as the monomer and BSB (which does not undergo the same type of elimination reactions as DiCumCl) as the initiator still resulted in molecular weights in threefold excess of the theoretical value. Despite the noteworthy improvement, initiator decomposition is not the sole reason for poor molecular weight control. ISI knows the reason for this behavior and the steps required to prevent it from occurring (confidential information).



Scheme 7

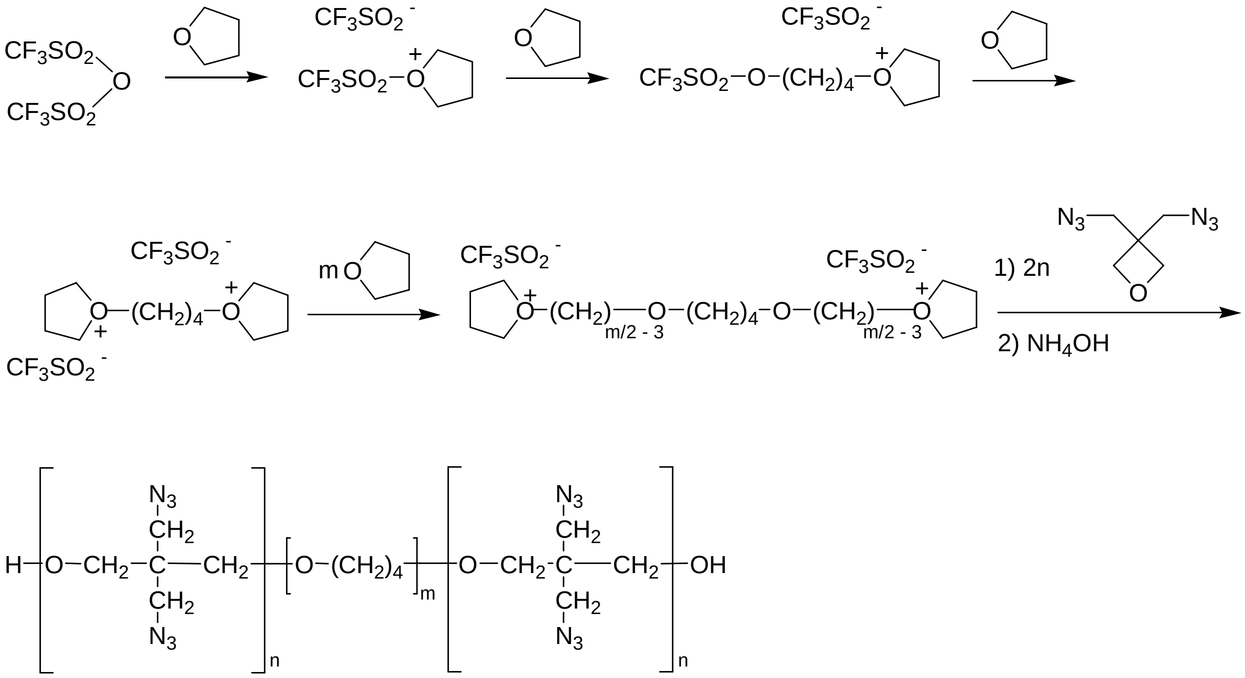


Scheme 8

The use of $AgSbF_6$ in conjunction with low polymerization temperatures makes this type of system impractical from a cost standpoint. A good knowledge of cationic polymerization is needed to understand the shortcomings of this initiator system. This coupled with unique insight into the cationic polymerization field allows ISI to overcome these problems in an environmentally friendly manner.

1.3 Covalent Initiators

Hsiue and co-workers[4] settled on an alternative polymerization system for the synthesis of energetic TPEs, based on work by Smith and Hubin[9] on the living polymerization of tetrahydrofuran (THF). Hsiue used triflic anhydride as a bifunctional initiator for sequential living block copolymerization of THF (inner, soft segment) and BAMO (outer, hard segments) in dichloromethane (Scheme 9).



Scheme 9

Analytical data supported the living nature of these polymerizations. For example, ^1H NMR and IR spectra for the resultant TPEs contained signals unique to both polyTHF and polyBAMO indicating a true block microstructure. Theoretical monomer ratios compared well with those as determined by ^{1}H NMR spectroscopic and GPC analyses. $\overline{M}_n$ approximated [M]/[I] and the PDIs of the resultant TPEs were relatively low (1.1 to 1.4). Although this polymerization system is well-behaved and allows for the synthesis of energetic polymers, it still requires the use of chlorinated solvents. ISI proposes innovative adaptations of this system that allow for its operation under less environmentally objectionable conditions.

In conclusion, a number of strategies for the ROP of EMs have been devised. Each method has limitations in control over polymer structure and/or operating conditions that prevents their commercialization. The factors that cause these deficiencies have eluded previous investigators and a good understanding of the cationic polymerization is required to identify them. ISI's expertise in this field allows it to recognize the actual variables behind these problems. Armed with this knowledge and innovative skills, ISI can provide solutions that overcome these faults in an environmentally sound nature.

Section 2: Research and Development Strategy

ISI has adopted a "Stage Gate" approach to maintaining objectivity in decision-making while keeping research projects organized on goal-oriented trajectories (Figure 1). Stages are

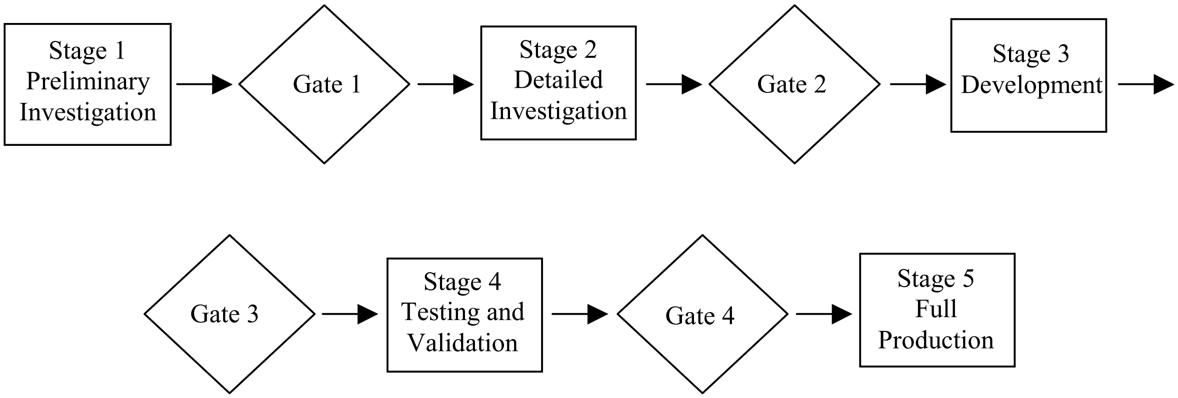


Figure 1

discrete research units with well-defined objectives. Gates are criteria for continuation. Normally, Gates must be fixed, pre-ordained metrics applied by managers or other agents external to the investigating team. However, in the context of this document, the definition of the Gate must be softened to acknowledge the diversity of practical problems facing MDC and the strong likelihood that ISI will not be able to provide a *single* solution to *several* problems simultaneously. Obviously one can achieve significant operational and economic advantages by making improvements in one area, even though improvements in several areas may be targeted. In particular, *reduced environmental impact*, especially the elimination of chlorinated solvents and highly toxic reagents, is a factor that could warrant some flexibility in the otherwise rigid Gate criteria because of its overarching importance from both economic and regulatory standpoints.

Stage 1

Preliminary Screening of ROP Methods. Using a single, representative energetic monomer (GN), the utility of several ROP systems will be investigated. This Stage is the most exploratory and will span variations in initiating system, solvent, and process conditions. Special attention will be given to ROP systems that enable rapid product recovery and solvent recycling, i.e., suspension polymerization techniques.

Gate 1

For an ROP method to be useful in TPE synthesis, molecular weight control is the most critical issue. Therefore the criterion for selecting successful ROP methods from Stage 1 will be *quasi-living* behavior in homopolymerization as determined by PDI and the proportionality of $\overline{M}_n$ to monomer/initiator ratio and to reaction time.

Stage 2

Scope of Selected ROP Methods. The utility of the preferred ROP methods for the homopolymerization of a variety of additional energetic monomers (i.e. BAMO, AMMO, NMMO) will be determined.

Gate 2

Successful ROP systems will demonstrate high productivity and quasi-living behavior across a broad spectrum of energetic monomers.

Stage 3

Extension of Homopolymerization Methods to Block TPEs. Each preferred ROP system will be examined for its effectiveness in producing TPEs using either direct block copolymerization or post-linking strategies.

Gate 3

For systems to merit further investigation they must exhibit at least two of the following:

A. Allow for preparation of energetic TPEs with desirable physical characteristics.

B. Cost efficient from a commercial standpoint.

C. Reduced environmental impact.

Stage 4

Testing and Validation. ISI will advise and assist MDC in scaling each preferred ROP systems to pilot plant scale.

Gate 4

The system that allows for the production of TPEs with desirable physical characteristics in the most cost effective manner under operating conditions that are desirable from commercial and environmental standpoints will move to the final Stage.

Stage 5

Production. MDC or a competent third party will implement the use of the fully developed technology on a commercial scale.

Section 3: Contractual and IP issues

3.1 Best Effort Basis for R&D

ISI acknowledges that one can never fully predict the outcome of research. Therefore, all deliverables are offered on a "best effort basis."

3.2 Reporting

ISI acknowledges that each Gate serves as the most logical point for reporting and for convening with MDC scientists and managers for joint decision making and planning. ISI will summarize and present all data to MDC in a professional and scientific manner within one month following completion of each Stage.

3.3 Intellectual Property and Licensing Agreements

It is anticipated that ISI and MDC will execute one or more non-disclosure agreements and then enter into a definitive consulting and development agreement based on the concepts and scope of work outlined in this proposal, which agreement may also have specific work orders associated with it. That definitive agreement and/or each specific work order will provide comprehensive provisions relating to intellectual property ownership and licensing ("IP Agreement"). With respect to that IP Agreement, ISI proposes the following concepts:

3.3.1 IP Definition

Intellectual Property shall include all inventions (whether patentable or not), patents, patent applications, copyrights, trademarks, trade secrets, and confidential information, including concepts, ideas, processes, compositions, software, methods, technical, financial, marketing, and business plans and information, strategic information, proposals, specifications, formulations and applications for such formulations, drawings, prices, costs, customer information, procedures, proposed products or applications of such products, techniques, services and like information.

3.3.2 IP Ownership

ISI and MDC shall each own all rights in Intellectual Property they have created, conceived or reduced to practice prior to this engagement (“Pre-existing Intellectual Property”).

With respect to work performed under the definitive agreement or a specific work order, unless otherwise agreed to in writing, ISI shall own all right, title and interest to Intellectual Property it conceives, develops or first reduces to practice (ISI Developed IP). In the event that ISI and MDC jointly develop, conceive or reduce to practice Intellectual Property (Jointly Developed IP), each party shall have an undivided half-interest in such Jointly Developed IP with, subject to any licenses granted, no duty of accounting to the other.

3.3.3 IP Licenses

The Agreement will have basic parameters around Intellectual Property licensing. At the time of each work order, the parties agree to negotiate in good faith for Intellectual Property licenses to ISI Developed IP or ISI Pre-existing IP, including, but not limited to royalties or license fees payable to ISI. Even in the event that an exclusive license is granted to MDC, ISI shall retain rights to practice under ISI Developed Intellectual Property for its own benefit. Finally, to the extent that MDC develops enhancements or improvements to ISI Developed IP, MDC shall provide a royalty-free license to such improvements, including the right to sublicense, back to ISI.

3.4 Budget

Each Stage requires a separate funding event from MDC. A simplified cost breakdown for Stage 1 for a full year of research is provided in Table 1.

Table 1, Cost Breakdown for Stage 1

Item description	Cost ($)
General operating costs (i.e rent)	8,000
Glassware/equipment	10,000
Chemicals	10,000
GPC/LLS	5,000
Spectral analyses (i.e. NMR)	7,000
Waste disposal	5,000
Miscellaneous	10,000
Legal/consulting fees	15,000
Salaries and fringe benefits	80,000
Total	150,000

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Abbreviations

AMI = all monomer in

AMMO = azidomethylmethyloxetane

BAMO = 2,2-bis(azidomethyl)oxetane

BEMO = 3,3-bis(ethoxymethyl)oxetane

BSB = bis(chlorodimethylsilyl)benzene

DiCumCl = *p*-bis(α,α-dimethylchloromethyl)benzene or dicumyl chloride

EP = energetic polymer

GN = glycidyl nitrate

GPC = gel permeation chromatography

I = initiator

IMA = incremental monomer addition

IP = intellectual property

IR = infrared

LALLS = low angle laser light scattering

M = monomer

MDC = Major Defense Contractor

$\overline{M}_n$ = number average molecular weight

$\overline{M}_w$ = weight average molecular weight

NMMO = 3-nitratomethyl-3-methyloxetane

NMR = nuclear magnetic resonance

PDI = polydispersity index or $\overline{M}_w / \overline{M}_n$

ROP = ring opening polymerization

ISI = Innovative Science, Inc.

THF = tetrahydrofuran

TPE = thermoplastic elastomer