

Polymerization of Glycidyl Nitrate via Catalysis with $BF_3 \cdot THF$: Compatibility with the Activated Monomer (AM) Mechanism

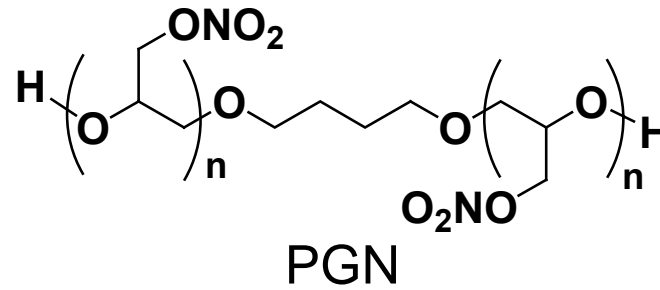
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PGN Overview

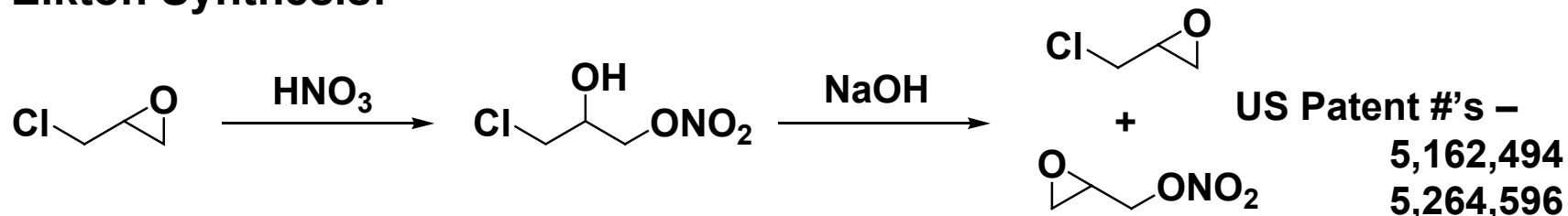


Density = 1.45 g/mL
 $\Delta H_f = - 68$ kcal/mol

- PGN is a liquid prepolymer which shows great promise as an energetic binder (high density, high oxygen content and favorable heat of formation)
- Binder formation occurs by reacting the prepolymer (-OH terminated) with isocyanate curatives, yielding elastic, energetic polyurethanes
- Target applications include minimum smoke propellants and high performance cast cure explosives
- ATK Thiokol has recently identified and exploited an inexpensive route to glycidyl nitrate from glycerin

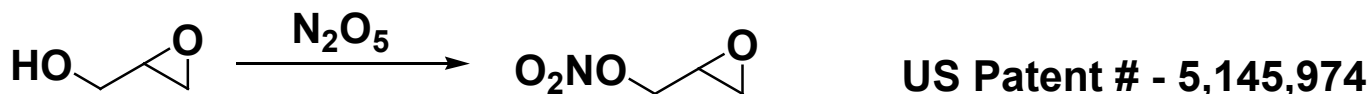
Glycidyl Nitrate Synthesis

Elkton Synthesis:



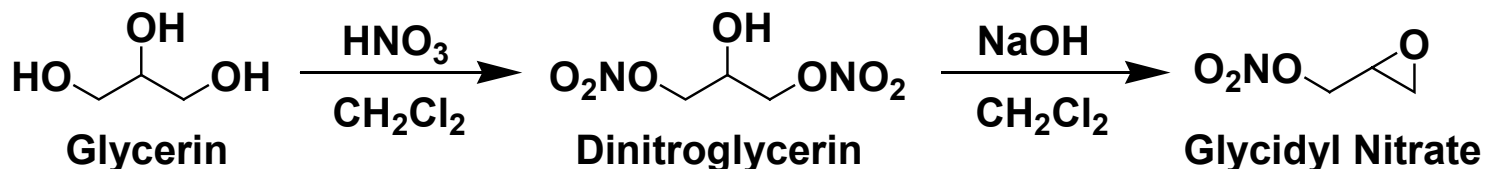
- Distillation of strained, cyclic nitrate ester required

ICI Synthesis:



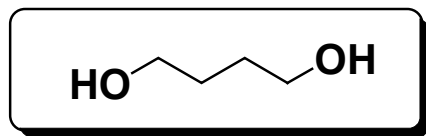
- Glycidol must be freshly distilled; starting materials are still not dirt cheap

ATK Thiokol, Inc. Synthesis:



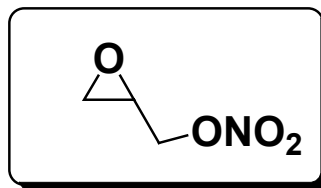
- Based on route reported by Naoum in 1907 US Patent # - 6,362,311
- Glycerin, nitric acid and sodium hydroxide (all inexpensive)
- Run as a continuous process (very amenable to scale-up)

Poly(Glycidyl Nitrate) Synthesis:



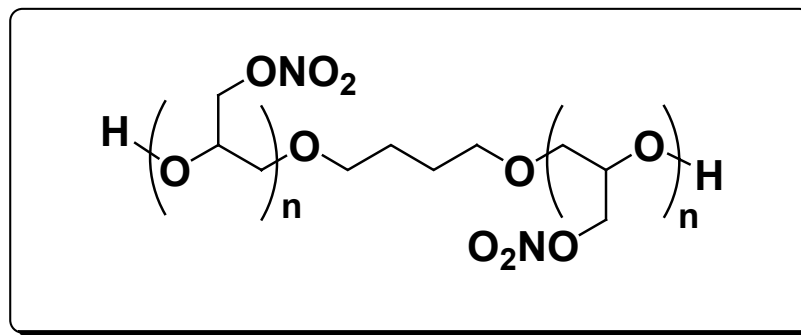
Initiator: 1,4-butanediol

+



Monomer: Glycidyl Nitrate

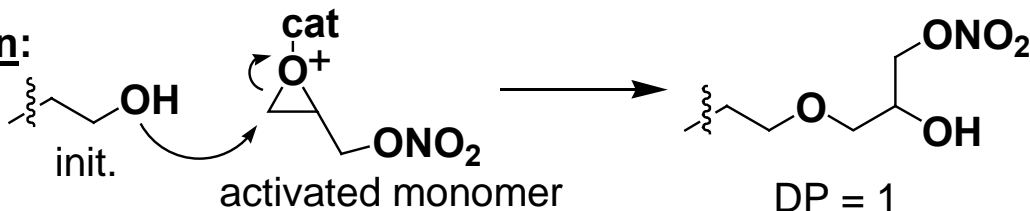
Catalyst: $\text{BF}_3\text{Et}_2\text{O}$, BF_3THF ,
 BF_3 (gas), PF_5 , SbF_5 , etc.



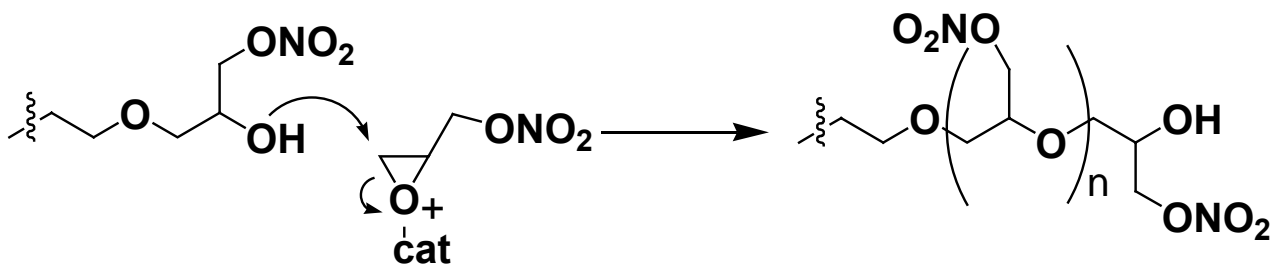
- Goals of PGN research:
 - Achieve higher, more predictable MW's (mechanical properties)
 - Make sure that the product cures reliably (functionality)
 - Make sure that the cured products are stable over time

Activated Monomer (AM) Mechanism* of GN Polymerization

Initiation:



Propogation:

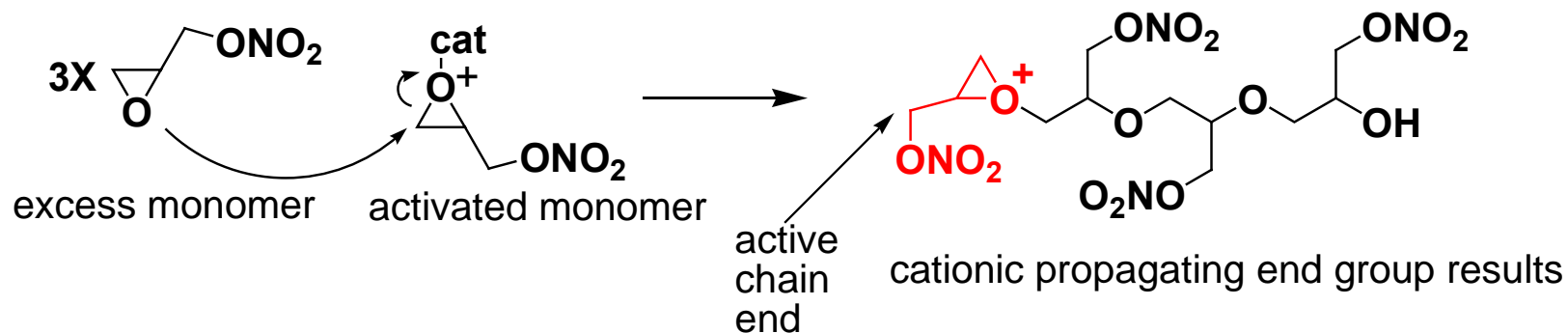


- Chain ends are inactive, so no cyclization or scrambling
- Should lead to quasi-“living” polymerization behavior (higher MWs, low PDI's, etc.)

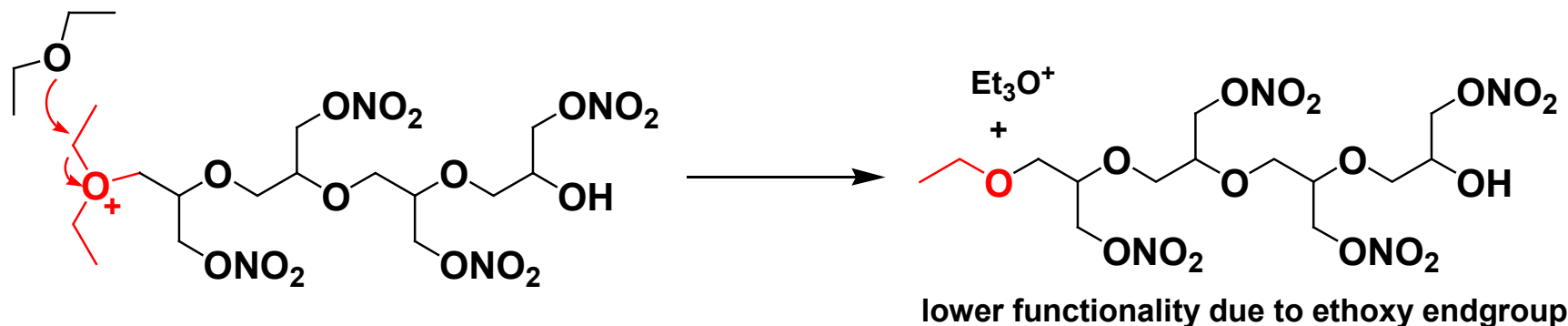
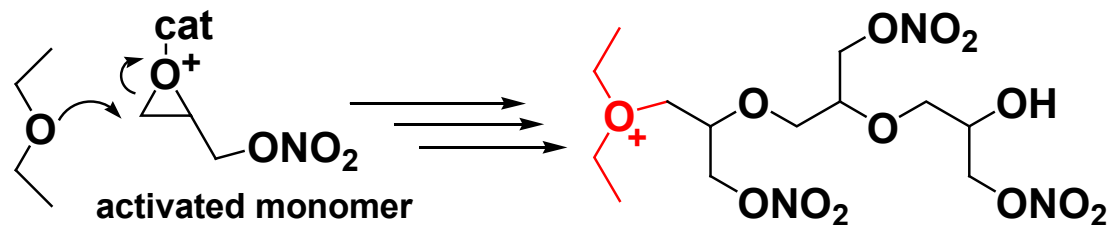
* Penczek, S. et al, *Makromol. Chem., Macromol. Symp.* **1986**, 6, 201

Uncontrolled Cationic Polymerization of Oxiranes: “Active Chain End” Mechanism

- Excess monomer leads to oxirane-initiated polymerization & active chain ends:



BF₃·Et₂O Catalyst : Leads to Active Chain End Mechanism and Chain Termination

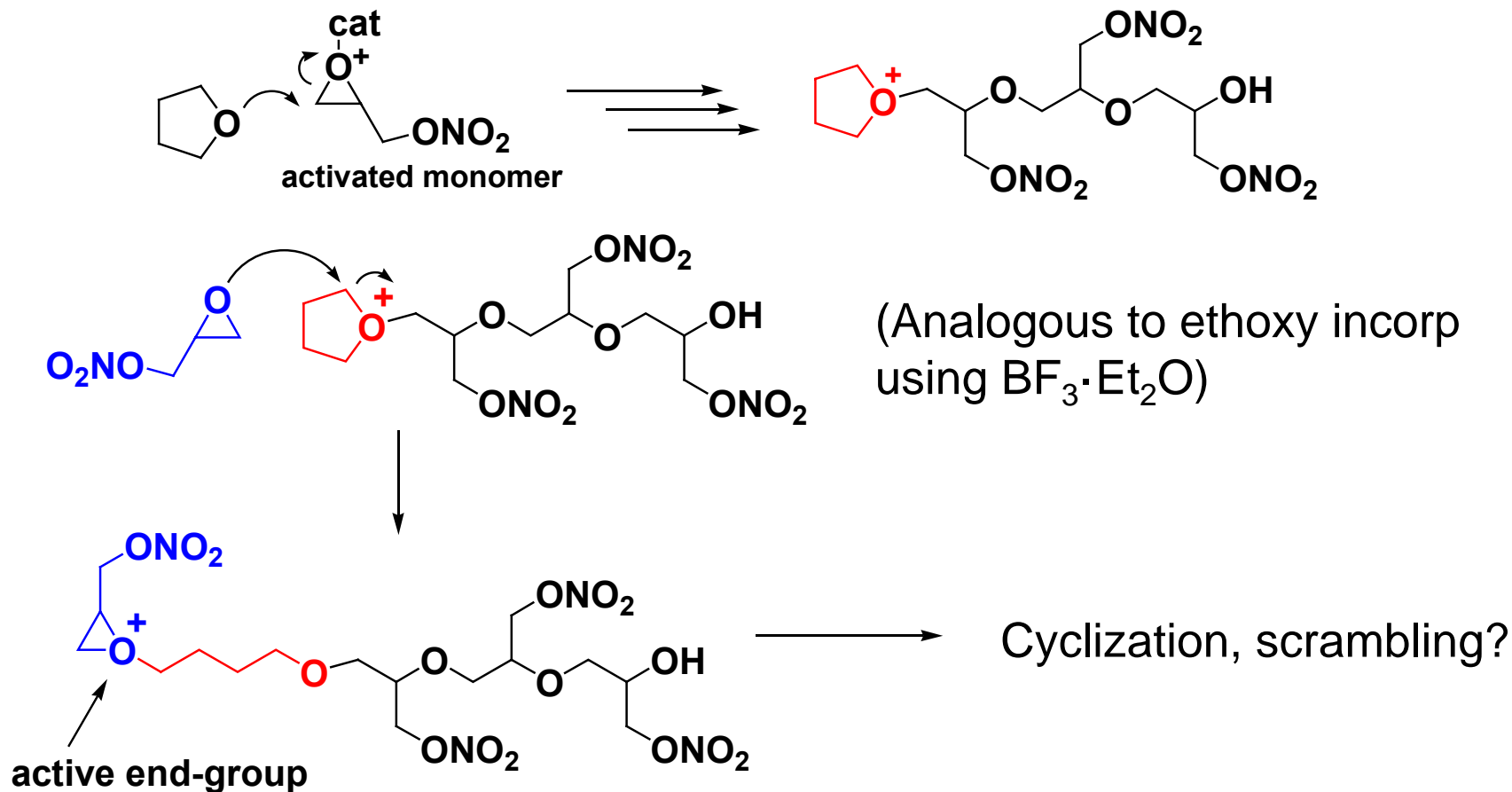


- Presence of diethyl ether leads to lower functionality PGN
- Began using other convenient BF₃-based catalysts (BF₃·THF)

BF₃·THF Catalyst

- BF₃·THF catalyst is relatively effective and does yield usable, reliable batches of PGN w/ high functionality
- However, THF initiates polymer growth, leading to lower MW's than targeted
- Polymerizations that were run w/ BF₃·THF in the absence of BDO initiator *still* exhibit BDO peaks in the ¹H NMR
- Less efficient active chain end mechanism is almost certainly involved, limiting the maximum attainable MW

Ring-Opening of THF Occurs *via* Active Chain End (ACE) Mechanism



-Perhaps absence of ethereal species will allow access to activated monomer mechanism and therefore higher MW's?

Alternate Catalyst Systems

- What happens with BF_3 -based catalysts in the absence of ethers?
- Two catalysts were tried:
 - BF_3 gas
 - Bubble gas through initiator, then begin monomer addition
 - $\text{BF}_3 \cdot \text{Et}_2\text{O}$ then vacuum
 - Add $\text{BF}_3 \cdot \text{Et}_2\text{O}$ to initiator, remove ether with vacuum, then begin monomer addition
- Experimental results:
 - No measurable difference between products formed using these catalysts compared to using BF_3 THF catalyst
 - All cure well (high functionality)
 - MW's reach a limit

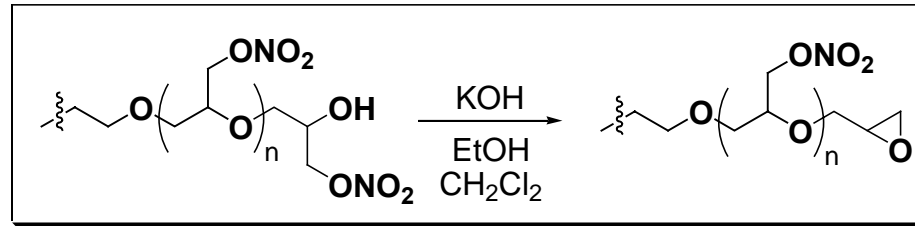
Data from Glycidyl Nitrate Polymerizations

Catalyst	Initiator	Target MW	M _n by GPC (THF vs PS)	NMR MW (Init:Repeat)
BF ₃ THF	1,4-BDO	5533	3037	4701
BF ₃ THF	1,4-BDO	5533	3584	4374
BF ₃ (vac)	1,4-BDO	10,802	3723	8738
BF ₃ (vac)	1,4-BDO	10,802	3214	9279
BF ₃ (vac)	1,4-BDO	6040	3147	5928
BF ₃ (vac)	1,4-BDO	4427	3123	3976
BF ₃ (gas)	1,4-BDO	7231	2707	6571

- The GPC M_n's are typically 2700-4000 g/mol
- The MW's as calculated by ¹H nmr (initiator:repeat ratios) disagree
- Which value is more accurate? (characterization)

Characterization of PGN

- Common methods for hydroxyl equivalent weight determination do not give reliable results with PGN (TFAA, TsNCO)
- Other methods of characterization?
 - Epoxide method of eq. wt. determination has been useful
 - Epoxidation of PGN is a well-known process (ICI/DERA)



- Quantitative endgroup conversion, reproducible results
- ¹H NMR of epoxidized PGN possesses three distinct epoxide peaks, which can be compared to those of the polymer repeat unit (reveals effective MW of parent PGN)
- Also reflects how much polymer is initiated via BDO vs initiated by other species

Epoxidation Results

Catalyst	Theor. MW	GPC M_n of PGN	GPC M_n of EpoxyPGN	NMR MW (init:repeat)	MW by Epoxy
BF ₃ THF	5533	3037	3217	4701	4260
BF ₃ THF	5533	3584	n/a	4374	4439
BF ₃ (vac)	10,802	3723	3270	8738	3307
BF ₃ (vac)	10,802	3214	3445	9279	3225
BF ₃ (vac)	8422	3662	2951	7736	3865
BF ₃ (vac)	6040	3147	2998	5928	3839
BF ₃ (gas)	7231	2707	3000	6571	3327

- MW's determined by epoxy-method tend to agree with GPC results as well as cure studies
- MW's determined by ¹H NMR init:repeat ratios do NOT appear to be reliable

PGN Cure Characteristics

- The cure characteristics of PGN depend largely on the isocyanate curatives used:
 - Gumstocks formed with aliphatic polyisocyanates such as N-100 possess good mechanical properties, but they do not age well (they deure over time)
 - Use of aromatic polyisocyanates (such as PAPI) with PGN results in gumstocks that age well but have compromised mechanical properties, due to low crosslink density (lower functionality of PAPI vs. N-100)
 - Our solution: start with higher functionality PGN
 - Use higher functionality initiators (trimethylol propane (TMP) or diglycerol (DG))

PGNs of Higher Functionality ($f = 3.0$ & 2.5)

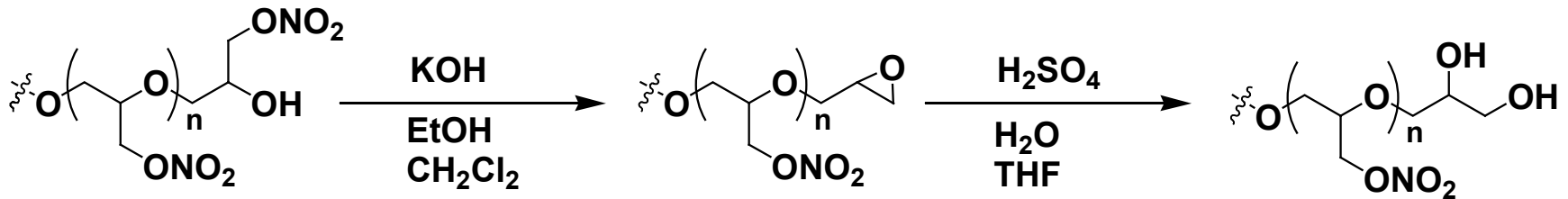
- Two alternatives were tried:
 - TMP-initiated PGN ($f = 3.0$)
 - Mix of 50% TMP and 50% BDO initiators (yields PGN with nominal $f = 2.5$)

Catalyst	Initiator	Theor MW	GPC M_n	NMR MW (init:repeat)	MW by Epoxy
BF_3 (vac)	TMP	10,802	3003	9900	4221
BF_3 (vac)	TMP	7231	2952	6357	3902
BF_3 (vac)	BDO/TMP	5347	3286	5437	3207
BF_3 (vac)	BDO/TMP	5467	2974	5467	3931
BF_3 (vac)	BDO/TMP	5467	2999	4777	4210

Cure Characteristics of Higher Functionality PGNs

- Both $f = 2.5$ and $f = 3.0$ PGN cure well with aromatic isocyanate PAPI
 - Tolerant of wider range of isocyanate : PGN ratios
 - Results in tougher cured materials (qualitatively), due to higher crosslink density of cured product
- However, these materials work well only with aromatic isocyanate curatives
 - Decure is still seen on aging when using aliphatic isocyanates such as N-100

“Fixed” PGN and Aliphatic Isocyanates



- Process developed by ICI and DRA Fort Halstead
- Modification procedure yields nominally tetrafunctional PGN
- Modified PGN possesses primary hydroxyl groups
 - More nucleophilic (react faster with isocyanates)
 - Forms stable urethanes with aliphatic as well as aromatic isocyanates
- We are currently investigating this option

Conclusions

- From a mechanistic perspective, BF_3THF is not an ideal catalyst for the polymerization of glycidyl nitrate
- However, *regardless* of catalyst used, we have experienced difficulty achieving MW's higher than 4000 g/mol
- PGN can be reliably produced w/ MW's of 3000-4000 g/mol
- PGN with $f > 2.0$ forms stable gumstocks with aromatic isocyanate PAPI, but not aliphatic isocyanates
- “Fixed” PGN forms stable gumstocks with aliphatic isocyanates, and we are actively investigating this approach
- The search for a method to produce higher MW PGN continues...

Activated Monomer (AM) Mechanism of Oxirane & Oxetane Polymerization

- Requires extremely low concentrations of monomer at all times (to avoid chain-end mechanism)
- Ideally, this mechanism leads to a “living” polymerization
- MW can be controlled by changing initiator : monomer ratio

* Penczek, S. et al, *Makromol. Chem., Macromol. Symp.* **1986**, 6, 201