Improving Efficiency and Limiting Side Reactions in ROMP-to-Anionic Polymerization Transformations

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Polymers and Copolymers

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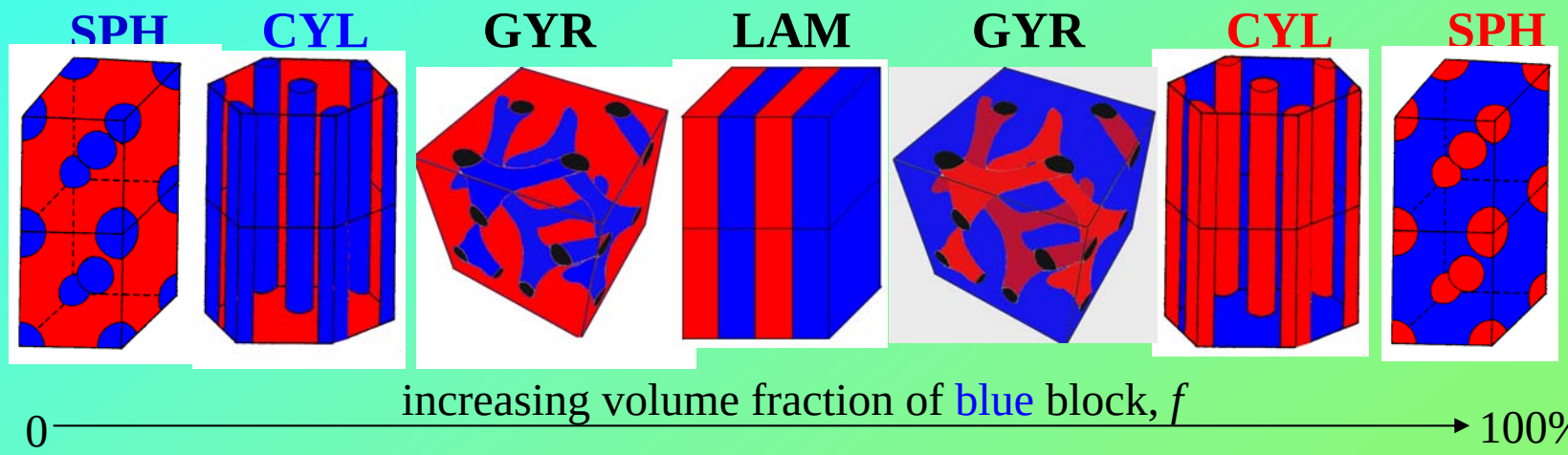
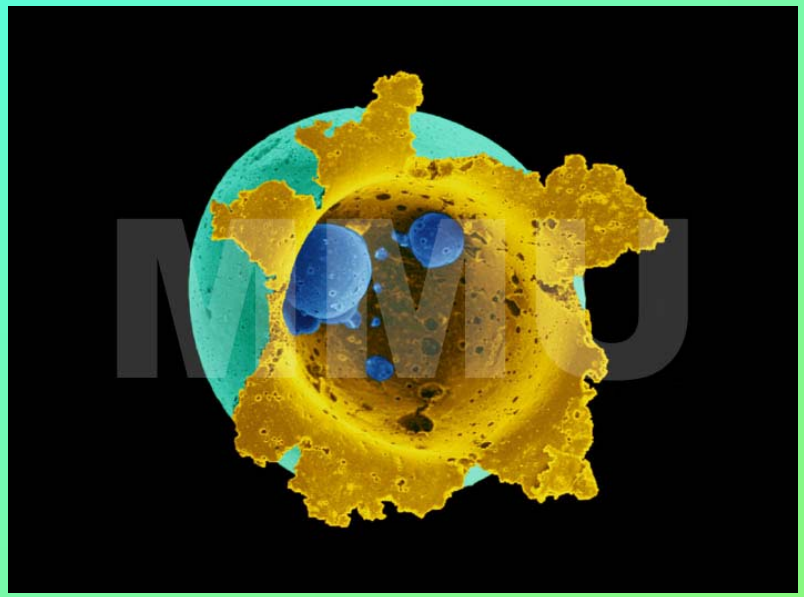
Monomer “A” Polymerization Polymer “Poly-A”



Polymer Applications

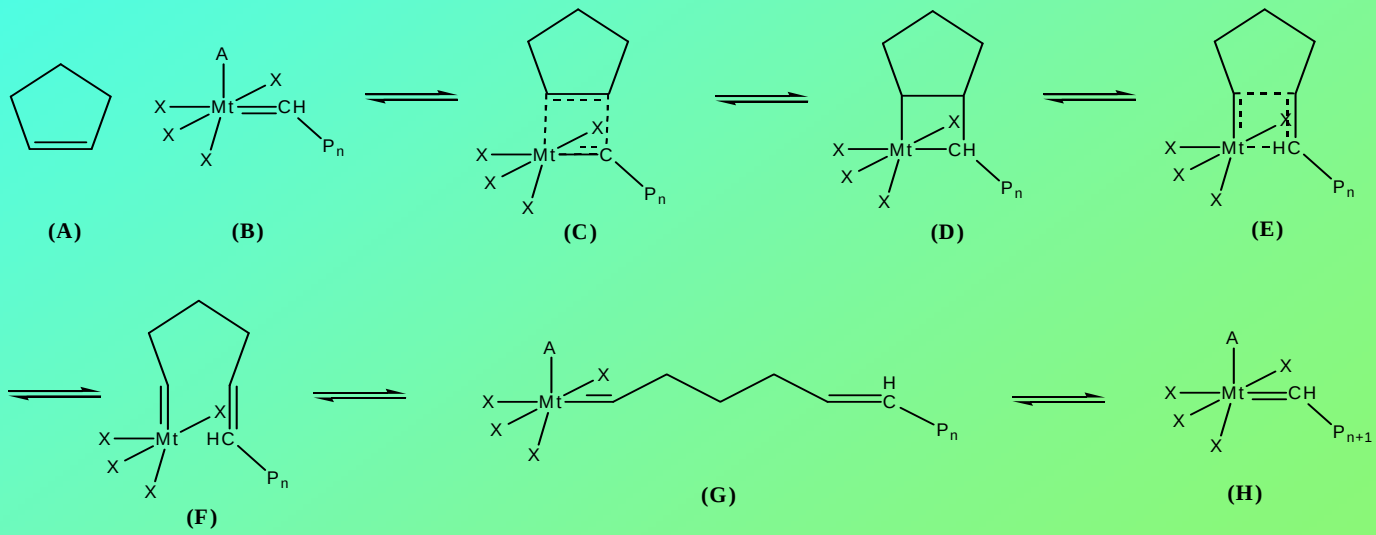


“Living” Polymerizations

- Chain growth processes that take place without chain breaking reactions like transfer and termination
- Result in well-defined polymers of controllable molecular weight and narrow molecular weight distribution (PDI<1.1)
- Two such examples are ROMP and Anionic polymerization

ROMP – Ring Opening Metathesis Polymerization

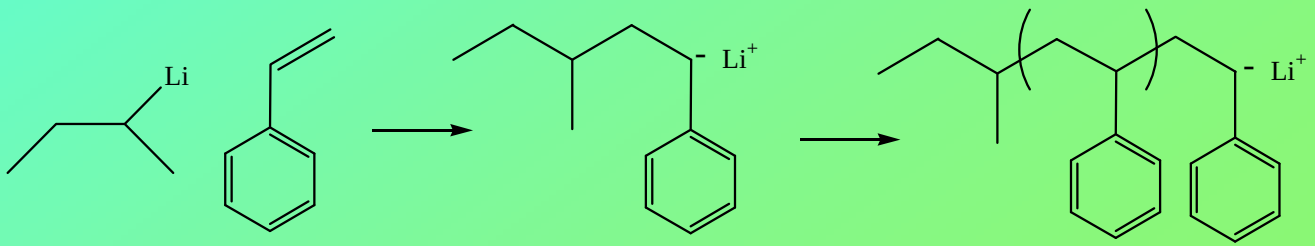
- Cyclic Olefins
- Unsaturation is conserved
- Release of ring-strain (>5 kcal/mol)
- Metal-mediated
- Equilibrium Controlled



Anionic Polymerization

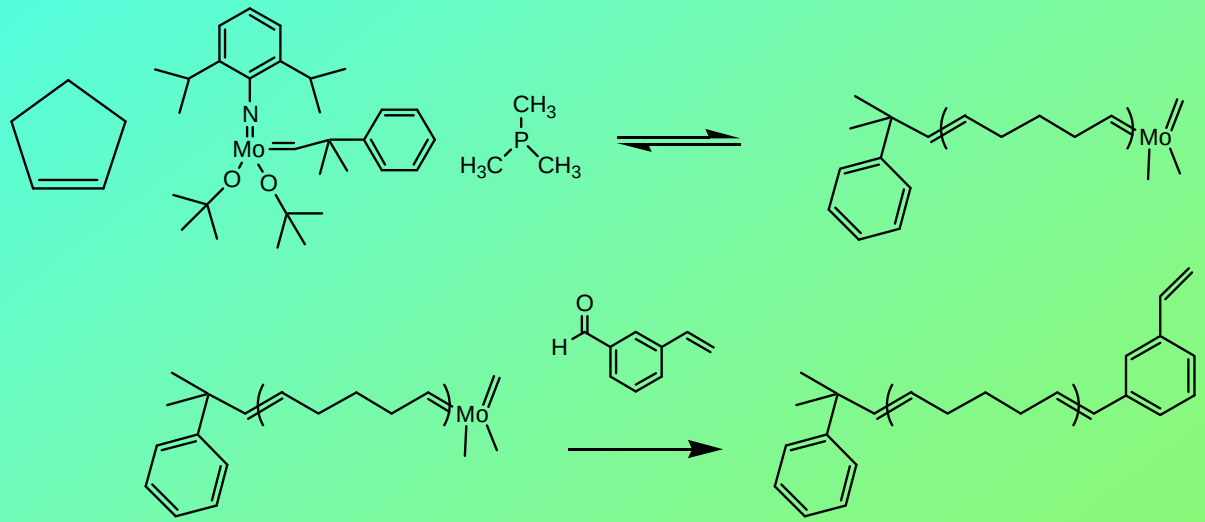
- Traditional ‘living’ polymerization
- Initiators are alkali metal complexes, typically alkyllithiums
- Usually monomers contain some form of double bond (vinyl or diene)
- Polarity of solvent controls initiation and polymerization rates and resulting polymer chain structure

styrene

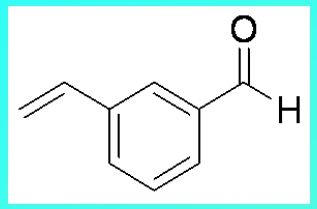


Versatility of ROMP/Anionic

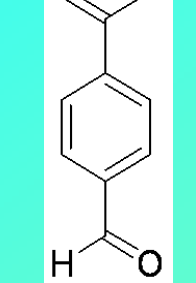
- Controllable molecular weights.
- Narrow molecular weight distributions and low PDI.
- ROMP alone has limited range of monomers
- Create well-defined block copolymers via anionic polymerization
- Combine ROMP and anionic to increase range of useful physical properties of copolymers



Change of Mechanism Agents

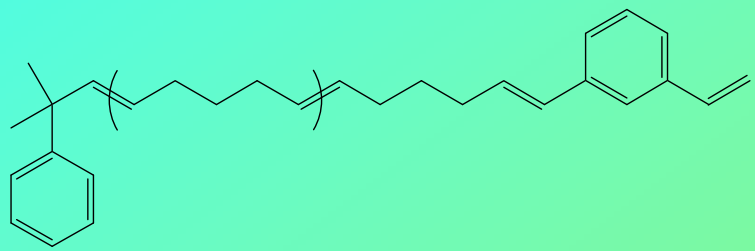


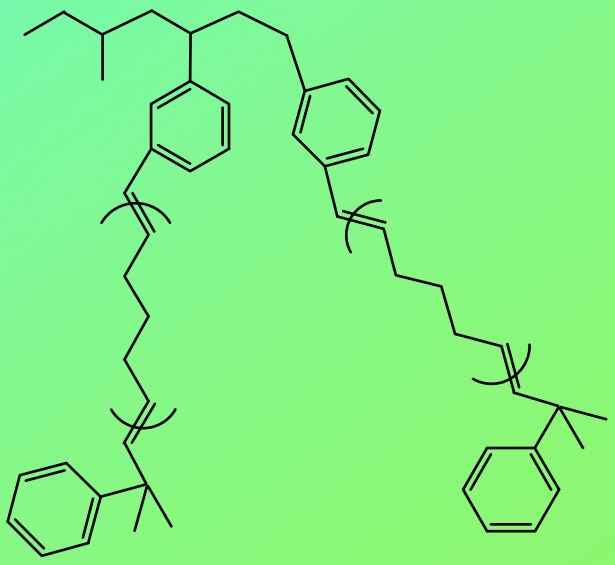
3-vinylbenzaldehyde



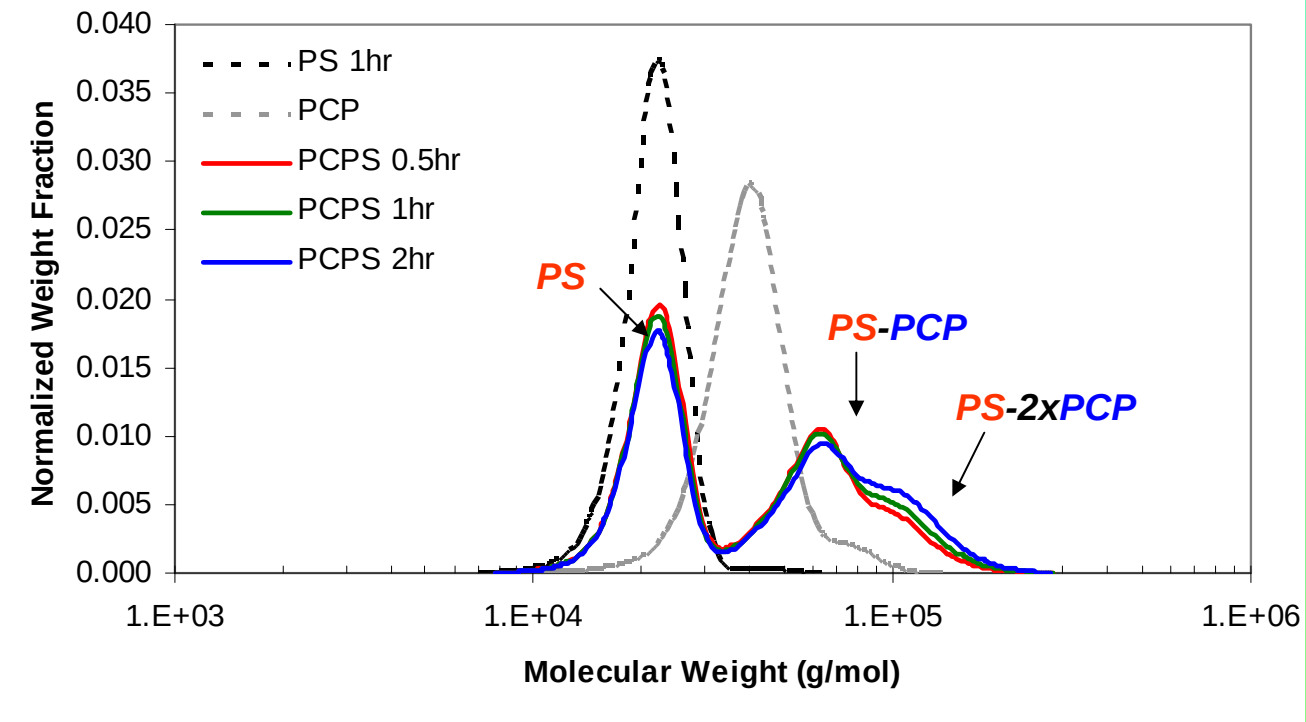
Isopropenylbenzaldehyde

- Not commercially avaliable
- Potential for limiting side reactions





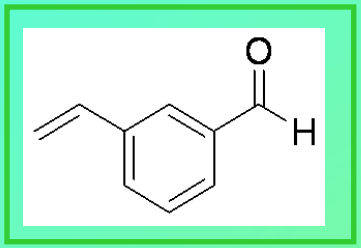
Problems with 3VBA

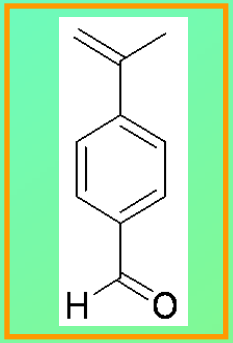


•Significant propagation of functionalized PCP resulting in the formation of PS-2xPCP and PS-3xPCP

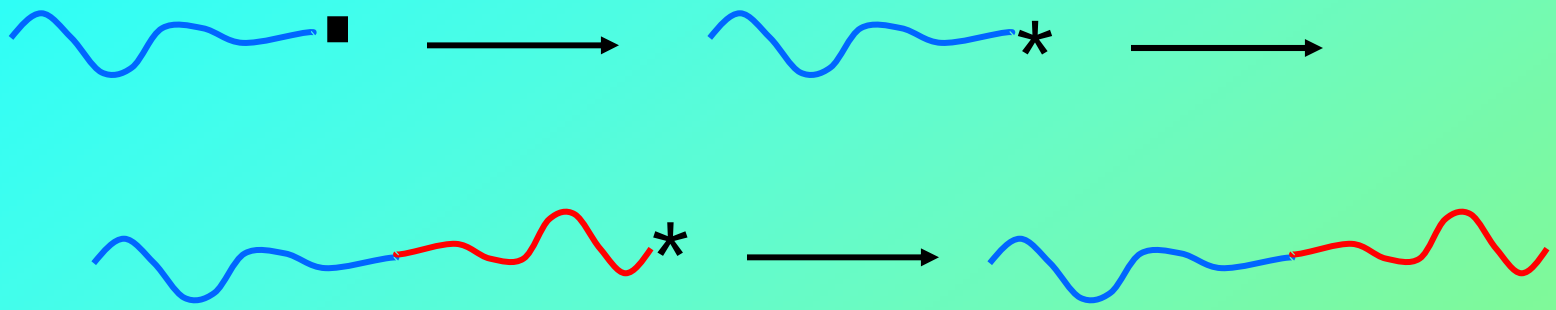
Project Goals

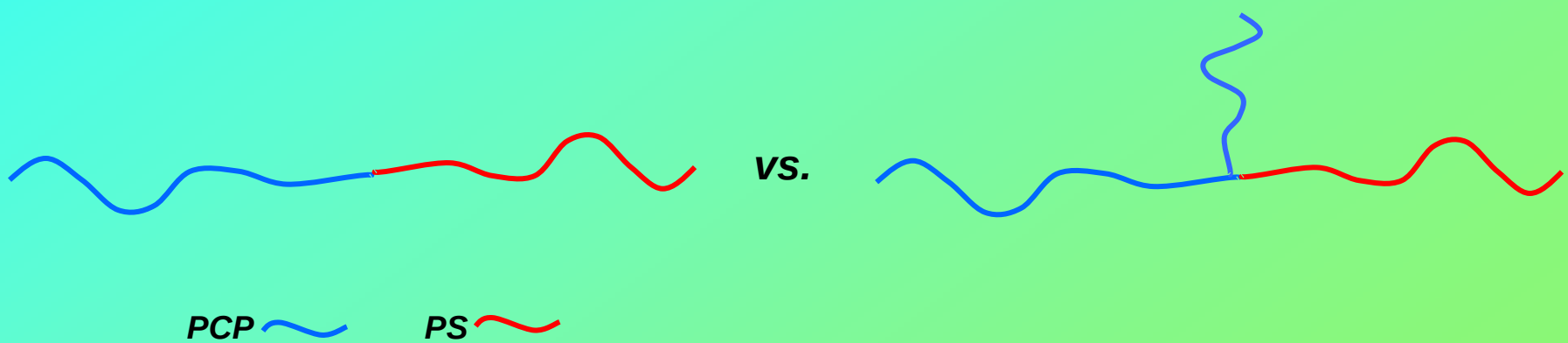
- Combine ROMP and anionic to increase range of potential monomers
- Eliminate unwanted side chains from adding to the polymer backbone
- Evaluate IPBA as a novel ROMP-to-AP change of mechanism agent
- Compare control reaction of 3-VBA- and IPBA-terminated PCP chains





Functional Terminating Agent

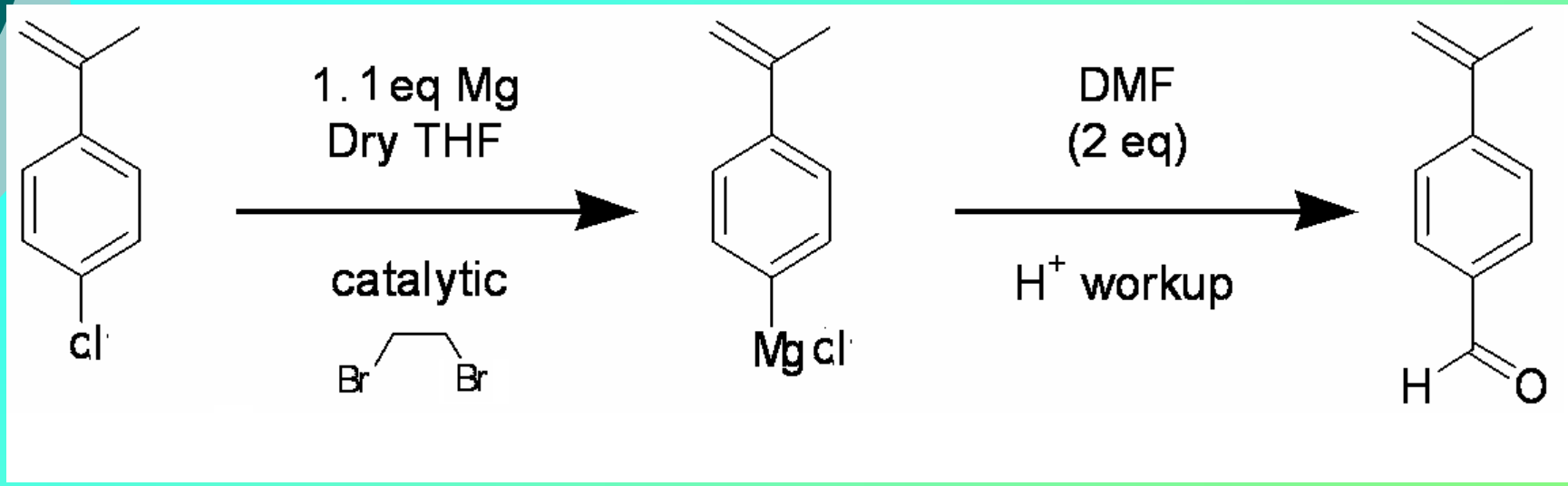




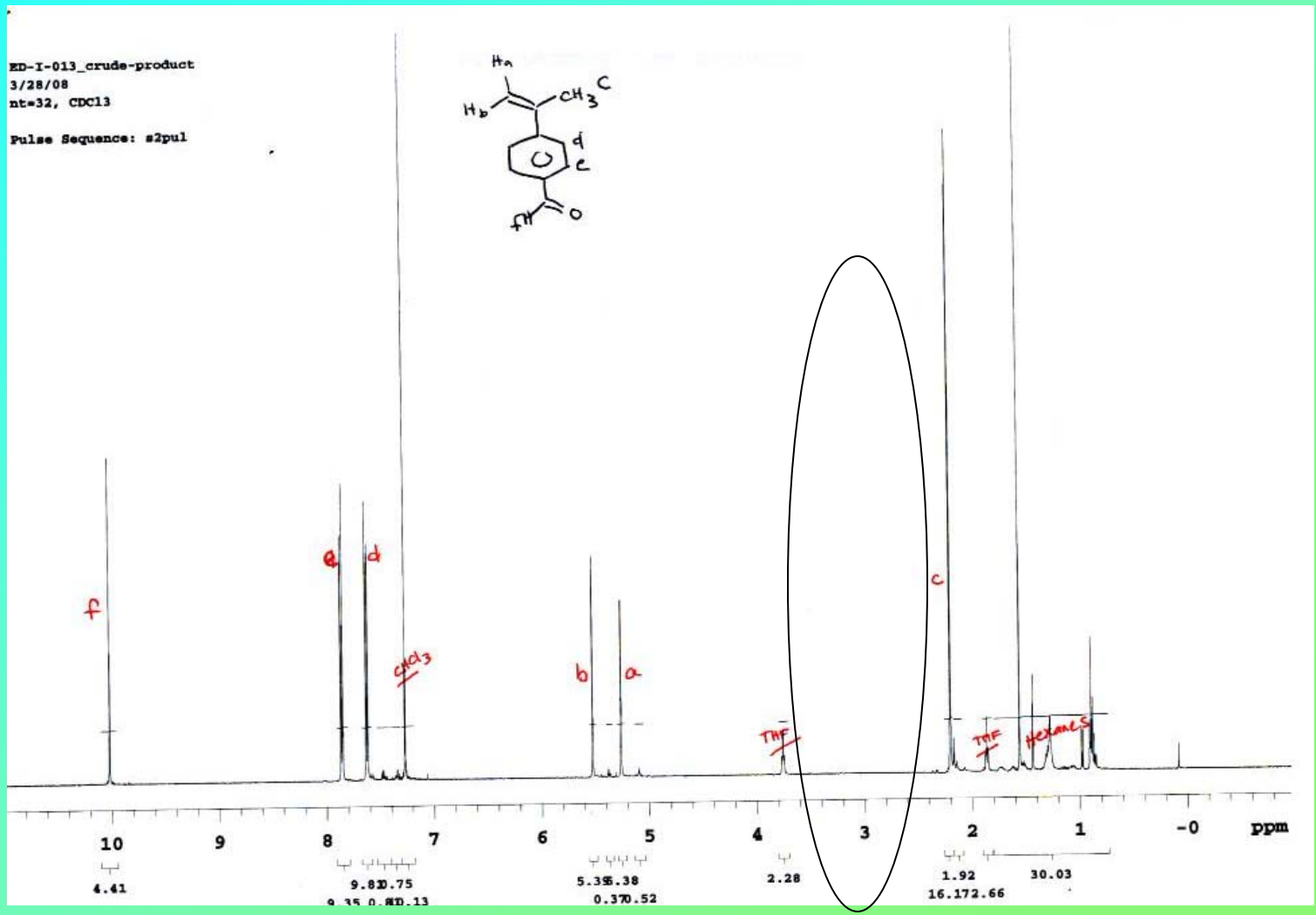
Materials and Approach

- Reagents “killed” by water and oxygen.
- Reaction amounts scaled to catalyst mass.
- Extraction and equilibrium.
- Reaction with functional terminating agent.
- Addition of anionic initiator and monomer.

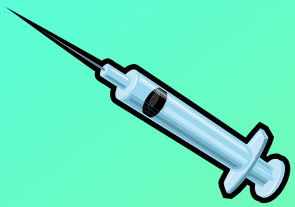
Synthesis of IPBA via Grignard Reagent

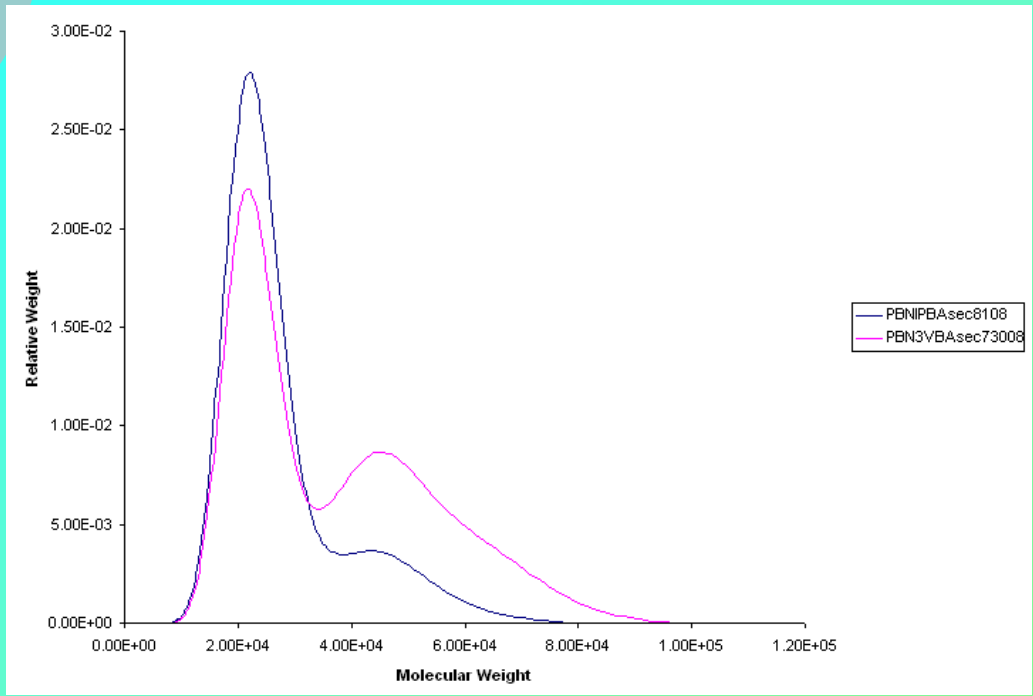


NMR (Nuclear Magnetic Resonance) Spectroscopy.



GPC (Gel Permeation Chromatography)





Sample	Mn (kDa)	Mw (kDa)	PDI
PBN3VBA	19.0	20.2	1.05
PBN3VBAs	19.8	21.1	1.06
PBNIPBA	19.8	21.4	1.08
PNBIPBAs	20.4	22.3	1.09

Project Future

- Anionic polymerizations of the terminated polybutylnorbornenes.
- NMR data and GPC of ROMP-Anionic polymers
- Comparison of 3VBA and IPBA in ROMP-Anionic
- Synthesis of IPPAA

Conclusion

- IPBA eliminates some unwanted side reactions
- IPBA is a better functional terminating agent than 3VBA

Acknowledgements

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