Ru-Based Catalyst for the ROMP Synthesis of Well-Defined Block Copolymers Containing Norbornene and Ethylidenenorbornene

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Background on Polymers and ROMP

- What is a polymer?

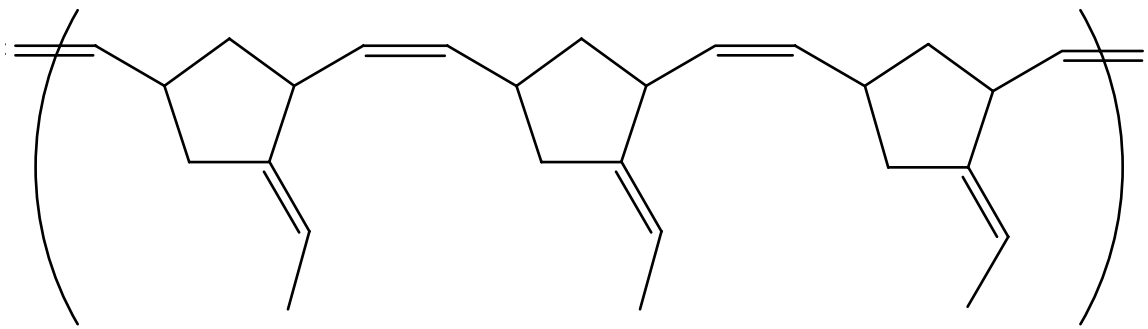
Macromolecules that are built up by the joining together of many smaller molecular units called monomers.

- Examples

  synthetic - plastics, polyester, nylon, teflon, polyethylene

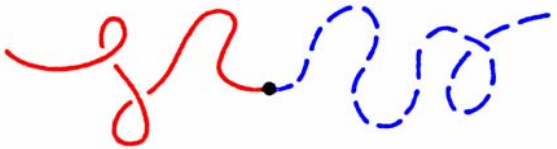
  natural – cellulose, rubber, protein, and DNA

Polyethylidenenorbornene

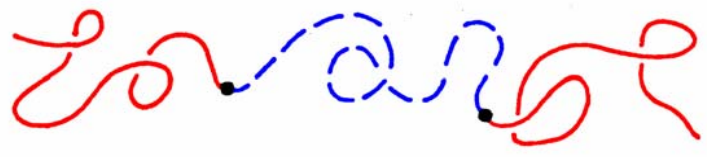


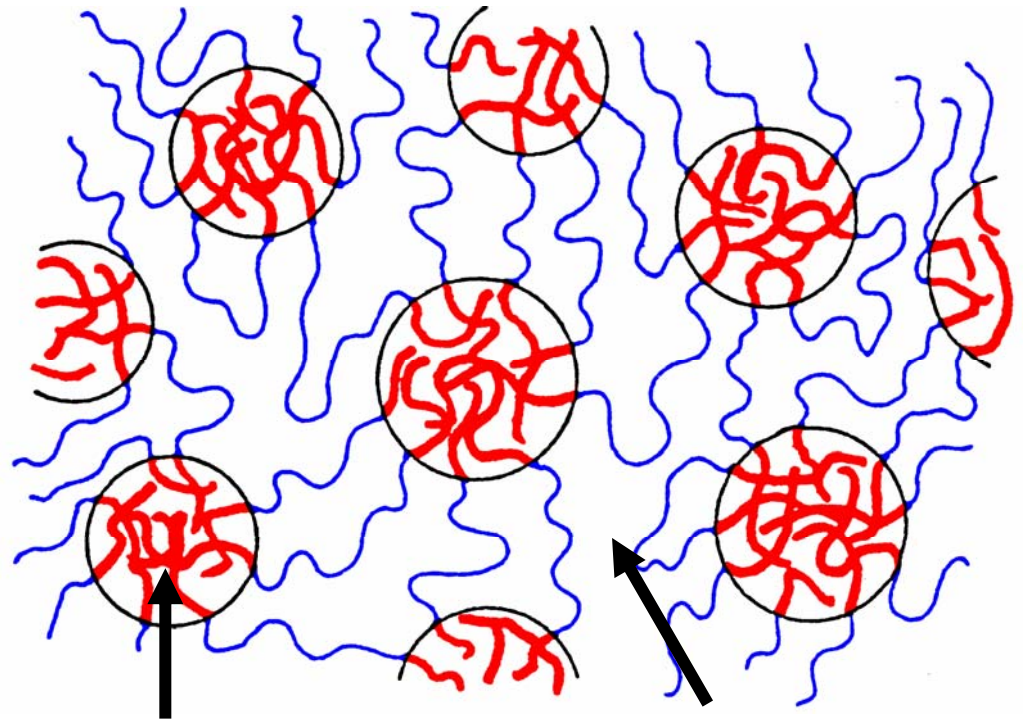
Block Copolymers

AB Diblock



ABA Triblock





A -- glassy spheres
(*e.g.*, polystyrene)

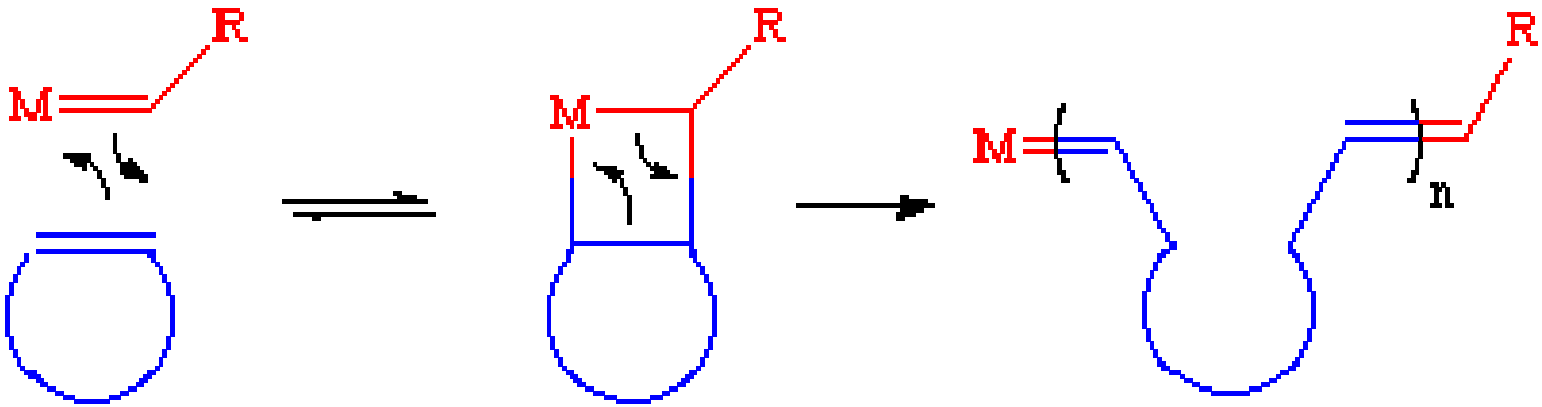
B -- rubbery matrix
(*e.g.*, polybutadiene)

Applications

- thermoplastic elastomers
- hot-melt adhesives
- toughening additives for plastics
- surfactants/rheology modifiers
- asphalt modifiers
- sealants and coatings
- nanostructured materials

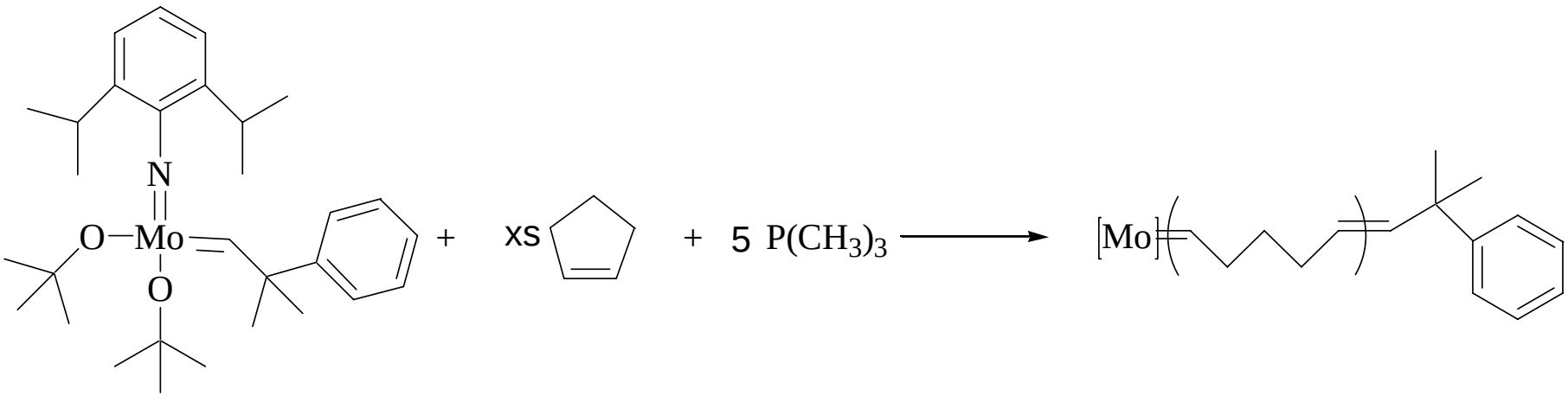
Ring Opening Metathesis Polymerization

- ROMP uses strained cyclic olefins to synthesize monodisperse polymers and copolymers.



- ROMP is an attractive method for making block copolymers.
  - A Living Reaction will continue indefinitely, until all the available monomers have been metathesized or until it is deliberately quenched by some terminating agent.
  - If initiation is significantly faster than propagation, it is possible for ROMP polymers to have a narrow range of molecular weights.

Molybdenum Catalyst and Cyclopentene



- PMe_3 binds reversibly to Mo center once bulky alkylidene unit is lost, slowing propagation relative to initiation and producing narrow molecular weight distribution, with PDI of less than 1.1

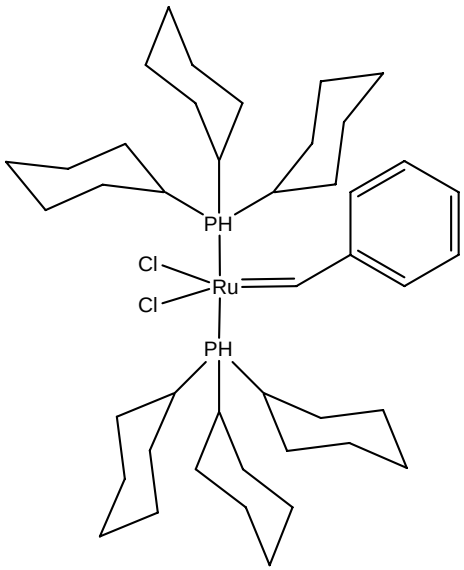
•S.T. Trzaska, L.-B.W. Lee, and R.A. Register, *Macromolecules*, **33**, 9215 (2000).

- However, when norbornene or its derivatives are polymerized with this ROMP catalyst, $P(CH_3)_3$ does not have the same effect because the ring opened norbornene is still large.

- A disadvantage of the Mo catalyst is its intolerance of oxygen, moisture and many functional groups.

Grubbs' Catalyst

• Grubbs' group at Caltech has developed a family of Ruthenium based ROMP catalysts, which are both more tolerant of functionality and significantly cheaper.

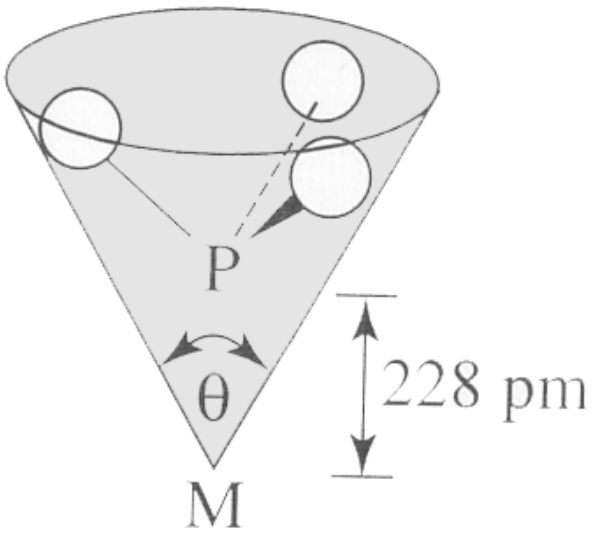


• The Ru catalyst reacts very rapidly, especially with the bicyclic monomers, resulting in a broad molecular weight distribution.

• We would be interested in using the Ru catalyst if polydispersity could be improved to same level as with the Mo catalyst.

• Is there a phosphine that could be used with the Ru catalyst that would slow propagation enough to improve polydispersity, but not so slow as to make the reaction unusable?

Cone Angles



• Cone Angle - the apex angle θ of a cone that encompasses the van der Waals radii of the outermost atoms of a ligand.

•For a phosphine ligands the dissociation constant can be directly related to cone angle.

• Ligands with large cone angles generally bond less strongly and are more easily dissociated from the metal center than are ligands with small cone angles.

• Which phosphine has the optimal size and chemistry to suit the Grubbs' catalyst?

Research Objectives

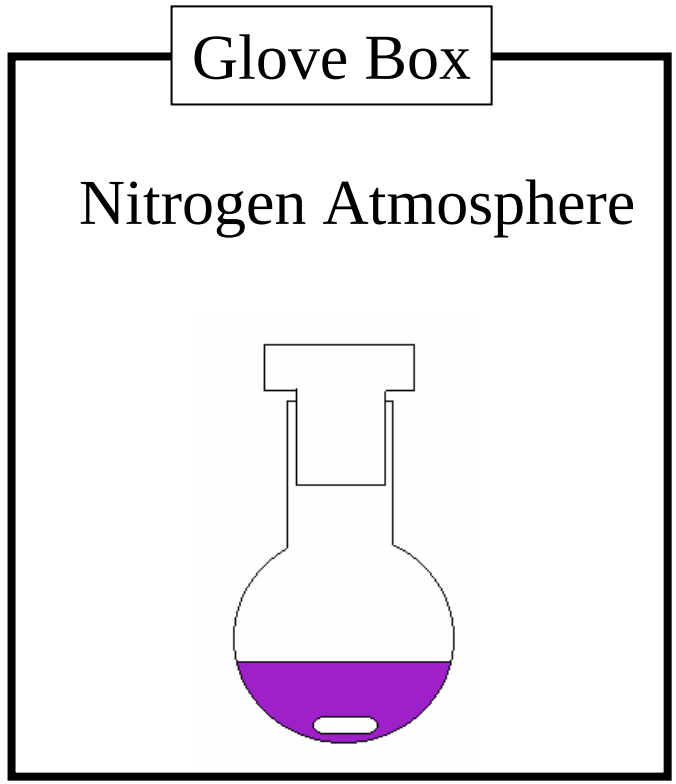
- Examine a variety of commercially available phosphines for their ability to suitably control the rate of propagation versus initiaiton, as determined by an improvement of the polydispersity when used with the Ru catalyst.

- For those phosphines which ‘show promise’ in improving the polydispersity, determine the optimal molar ratio between catalyst and phosphine.

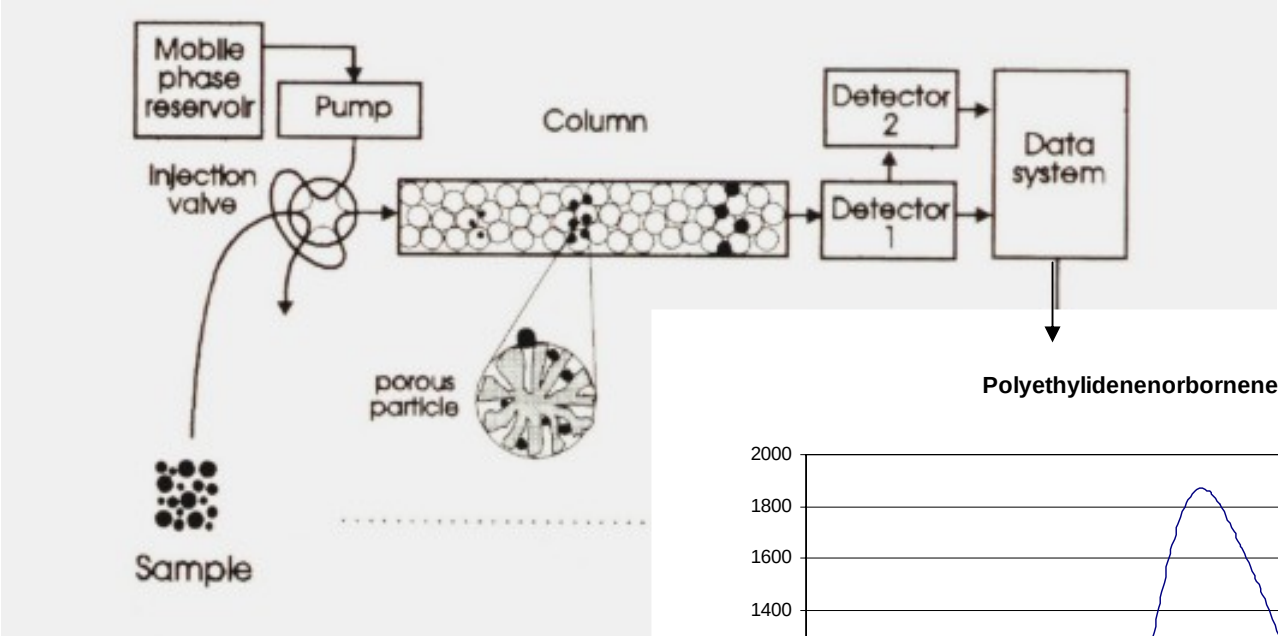
- Once a phosphine/catalyst combination has been found to improve the MWD with the initial monomer, determine its effectiveness in polymerizing other monomers, such as norbornene and cyclopentene.

Experimental Procedure

- All polymerizations were carried out in a 50 ml round bottomed flask with constant stirring in a glove box with a nitrogen atmosphere.
- All glassware was flamed out before entering the glove box.
- Reactions were timed and quenched with benzylaldehyde after one hour.
- Polymer product was separated and purified by precipitation in methanol.
- Polydispersity was then measured using Gel Permeation Chromatography.



Gel Permeation Chromatography

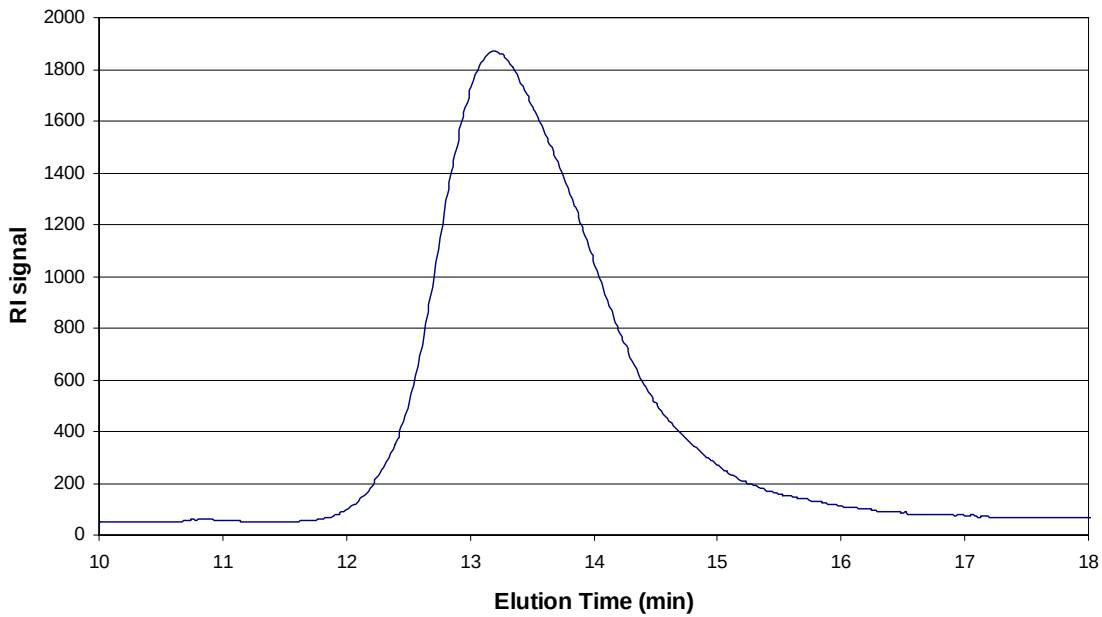


GPC separates polymer molecules according to size which is a function of molecular weight

Large molecules move quickly through the column.

Small molecules move slowly as they penetrate the pores.

Polyethylidenenorbornene / Ru Catalyst / PDI 1.76

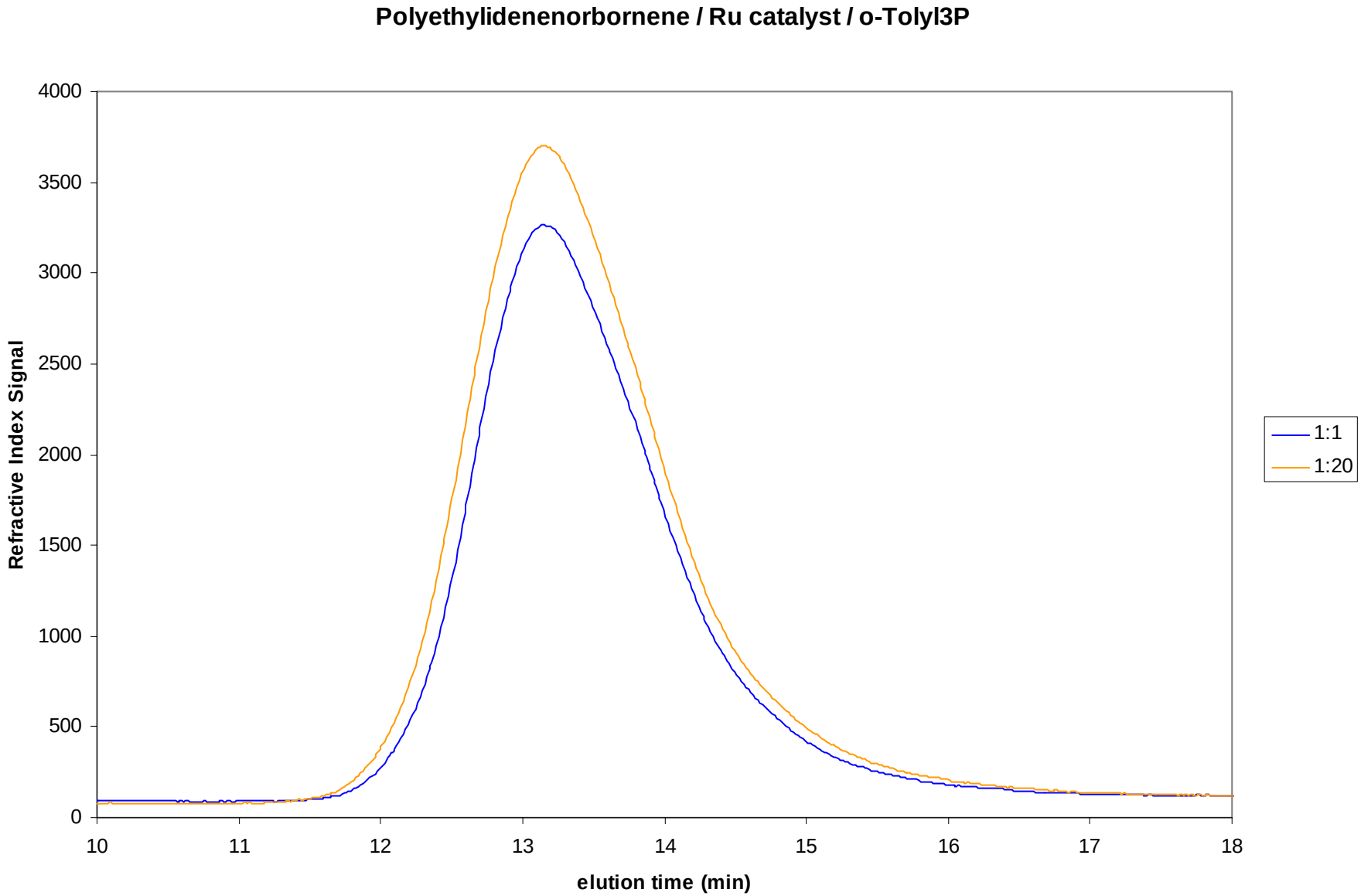


Experimental Results

- As expected the phosphines' ROMP activity could be qualitatively correlated to cone angle. The smaller ligands, including trimethyl-phosphine, inhibited the polymerization of ethylidenenorbornene, whereas the largest, tri-o-tolylphosphine, did not seem to have any affect on the reaction.

Phosphine		Cone Angle	ROMP result
$P(Me)_3$	trimethyl	118	no polymer
$P(Pr)_3$	tri-n-propyl	132	no polymer
$P(n\text{-}Oct)_3$	tri-n-octyl	~132	no polymer
$P(Ph)_3$	triphenyl	145	narrowed MWD
$P(c\text{-}C_6H_{11})_3$	tricyclohexyl	170	narrowed MWD
$P(o\text{-}MeC_6H_4)_3$	tri-o-tolyl	194	broad MWD

Gel Permeation Chromatography



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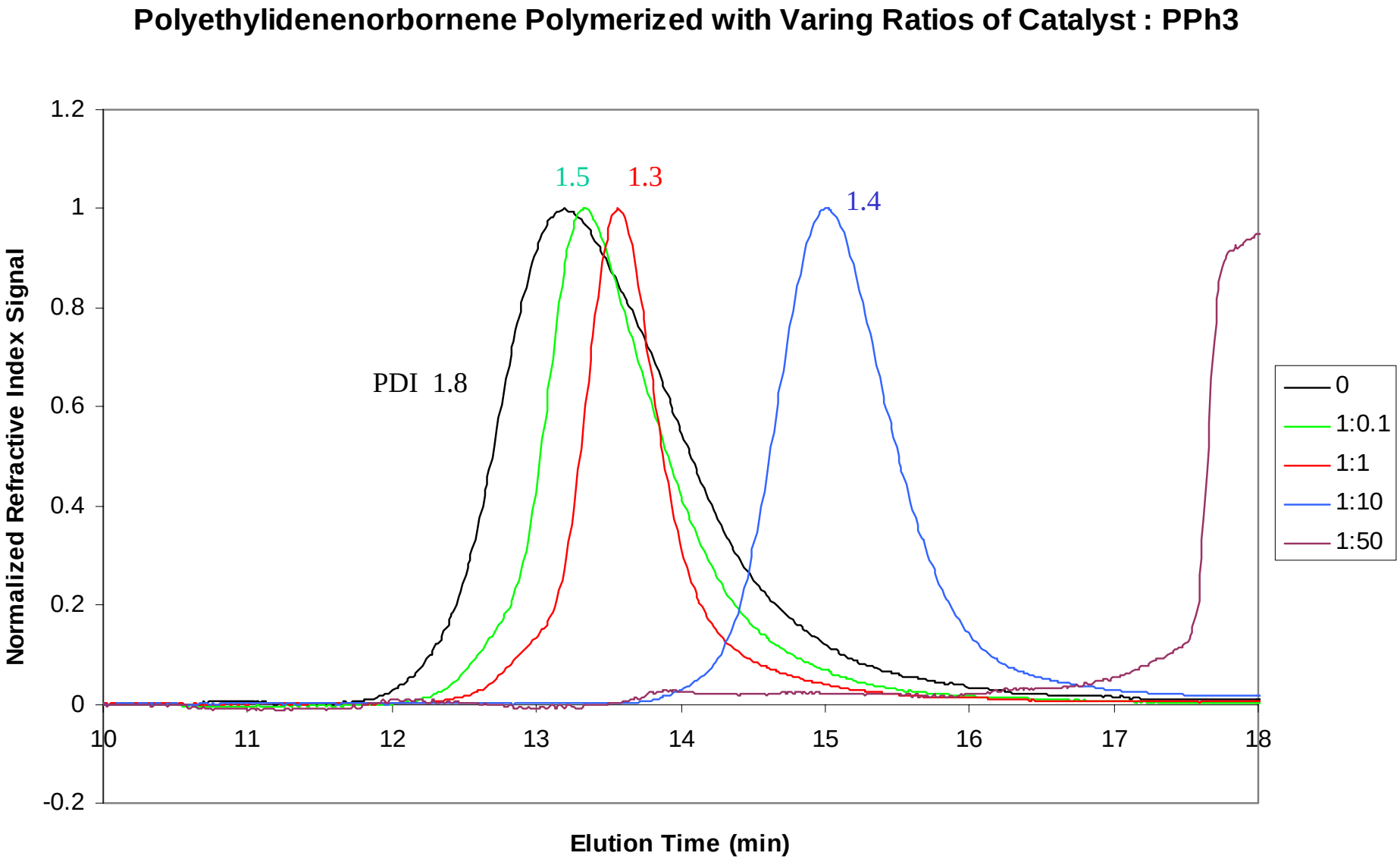

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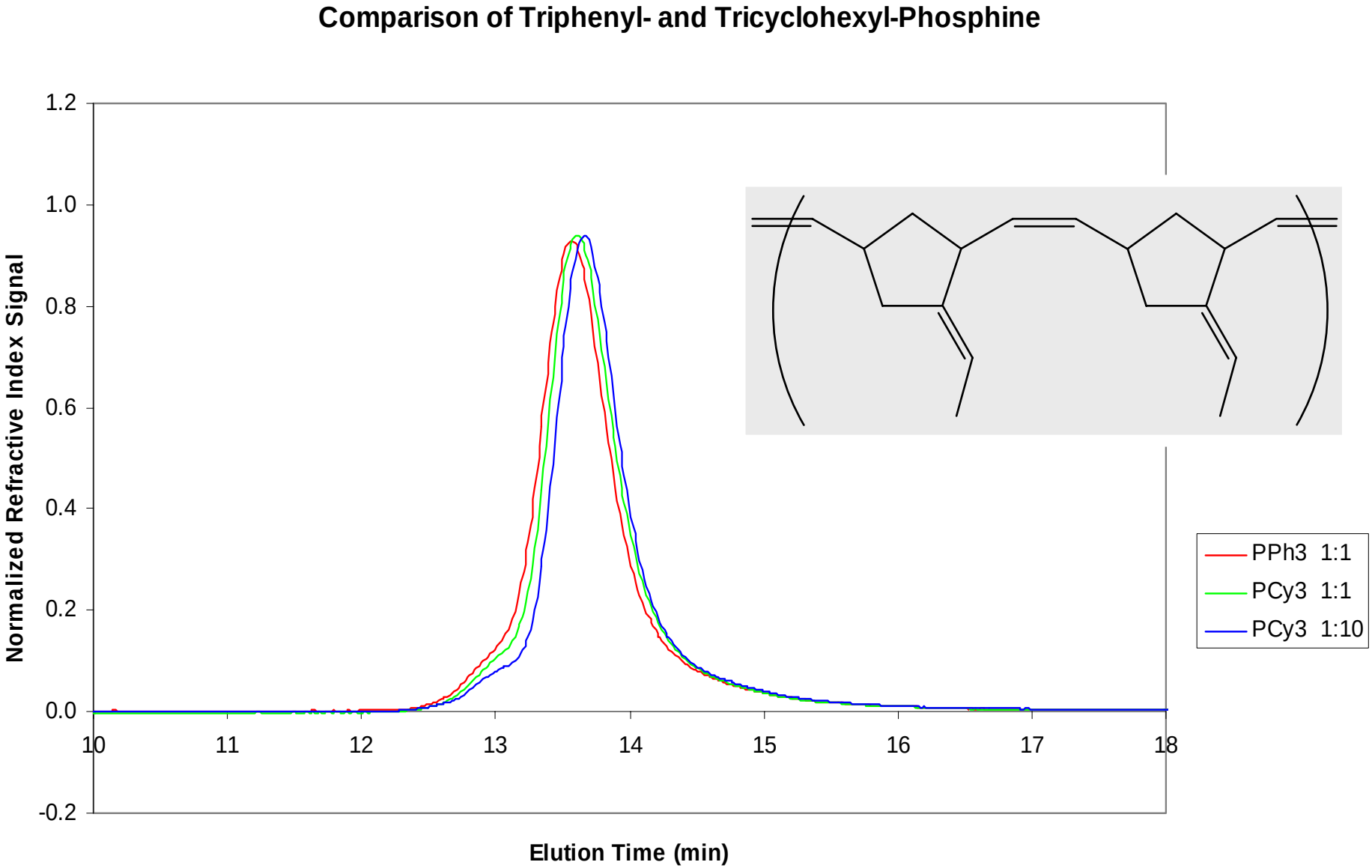

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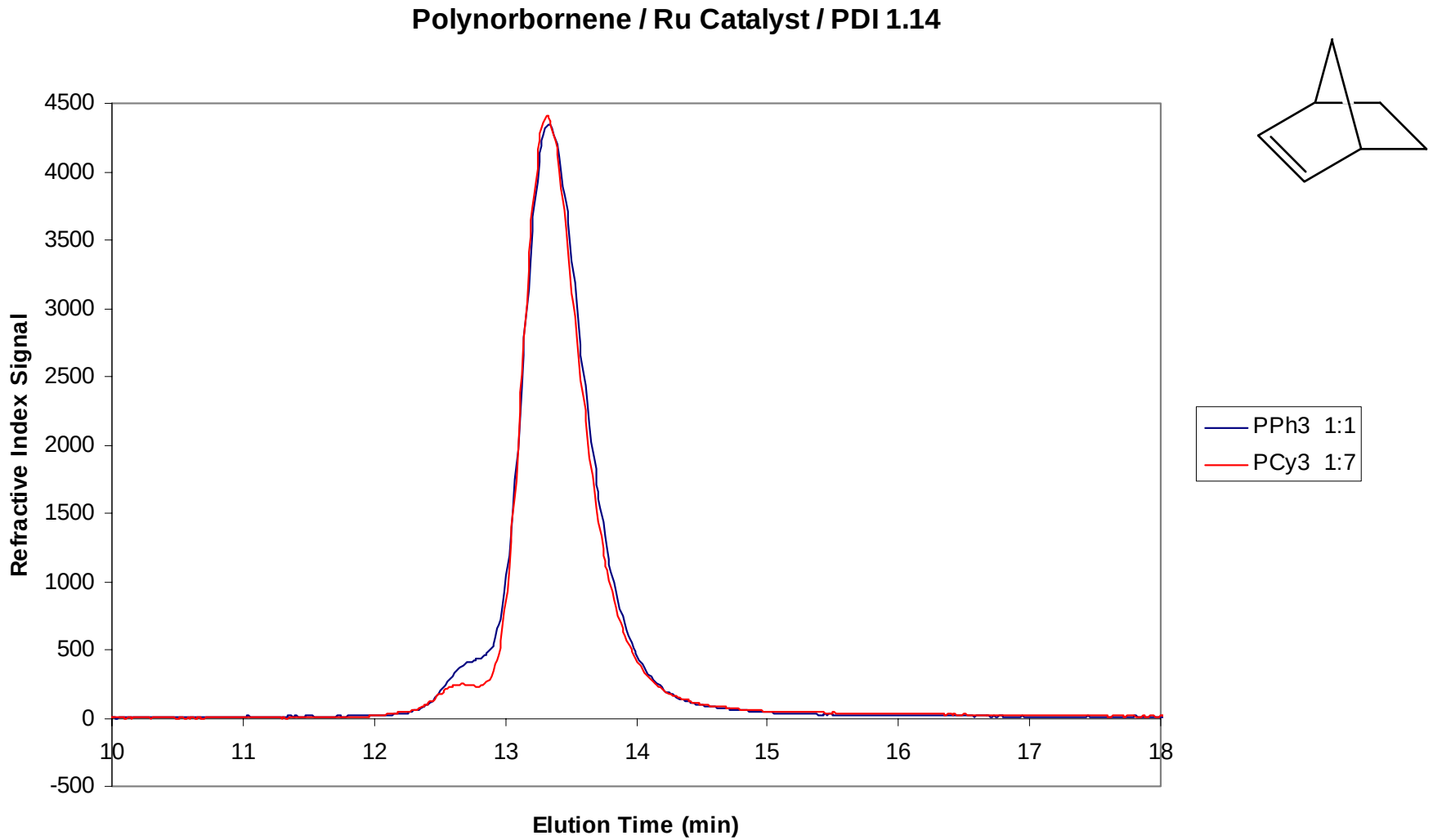

Conclusions

- The relative size of a phosphine ligand, as measured by cone angle, directly affects its ability to interact with the Ru catalyst and therefore its effect on the rate of propagation.
- The polydispersity of polyethylidenenorbornene, when polymerized with the Grubb's catalyst, was significantly improved by the addition of certain phosphines.
- Triphenyl- and tricyclohexyl- phosphines both showed approximately the same narrowing of molecular weight distribution with both polynorbornene and polyethylidenenorbornene. However, the polydispersity was still greater than what could be achieved with the Mo catalyst.
- Further exploration of the phosphines in the range of 140-180 degrees, including those with a greater variety of heterogeneous and branched chain alkyl and aryl groups, could lead to a phosphine which further improves the polydispersity when using the Grubbs' catalyst.

Acknowledgements

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Chemical Structures