

TECHNOLOGY TUTORIAL

The Chemistry of Norbornene Monomers and Polymers and
Products and Application Areas



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Subsidiary of Sumitomo Bakelite Co. Ltd.

Overview

- What is Norbornene?
- What are Functionalized Norbornene Monomers?
- How are Norbornenes Polymerized?
- Promerus Proprietary Catalysts
- Customization of Polynorbornene Polymers
- Products and Application Areas



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Promerus LLC is a Leader in Polycyclic Olefins

- We have 25+ years of Polynorbornene R&D and commercialization experience
- Our research and development efforts include:
 - ✓ Catalysis Research
 - ✓ Monomer Synthesis and Production
 - ✓ Polymerization Activities
 - ✓ Formulation Development
 - ✓ Application Validation
- We deliver a unique platform of materials for electronics packaging and other applications



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What Is Norbornene?

Norbornene is a bicyclic olefin.

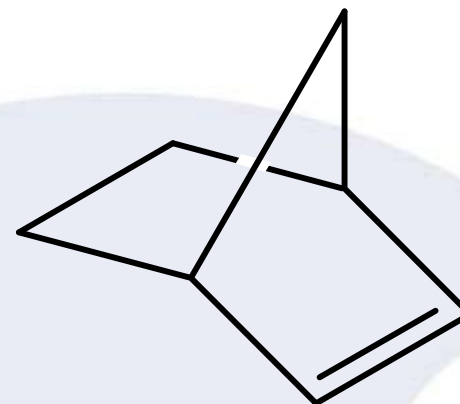
Norbornene possesses ring strain, so the molecule contains a highly reactive double bond.

Norbornene is manufactured via the Diels-Alder reaction of cyclopentadiene and ethylene.

Norbornene is a colorless substance that melts at 46° C.

Norbornene finds use in many different applications:

- ✓ Cyclic Olefin Copolymers (COC)
- ✓ Pharmaceutical intermediates
- ✓ Pesticide Compounds
- ✓ Specialty Fragrances
- ✓ General Organic Synthesis



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What are Functionalized Norbornenes?

Functionalized norbornene monomers are typically prepared via either high or low temperature Diels-Alder-reactions, and via derivatization.

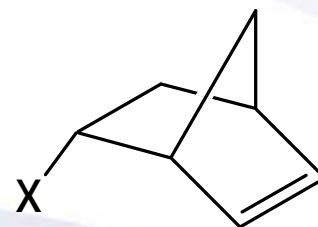
High purity, functionalized norbornenes can be as reactive as norbornene.

Functionalized norbornene molecules exist as two isomers: endo (major) and exo (minor).

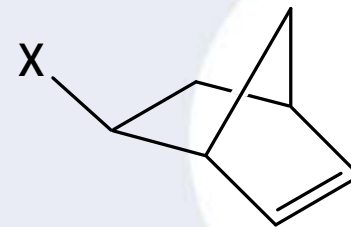
Many high purity, functionalized norbornenes are liquids.

Functionalized norbornenes contain many different types of reactive and non-reactive groups. Example substituents include:

- ✓ Acetate (OC(O)R)
- ✓ Alcohol (OH)
- ✓ Alkyl (R)
- ✓ Aldehyde (C(O)H)
- ✓ Anhydride (RC(O)O(CO)R)
- ✓ Epoxide (CH₂C(O)CH)
- ✓ Ester (CO₂R)
- ✓ Ether (OR)
- ✓ Ketone (C(O)R)
- ✓ Nitrile (C≡N)
- ✓ Silyl Ether (Si(OR)₃)
- ✓ Phenyl (Ar)



endo isomer



exo isomer



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Diels-Alder Chemistry is Used to Prepare Norbornene Monomers

Natural Gas

Ethylene

Propane,
Propylene

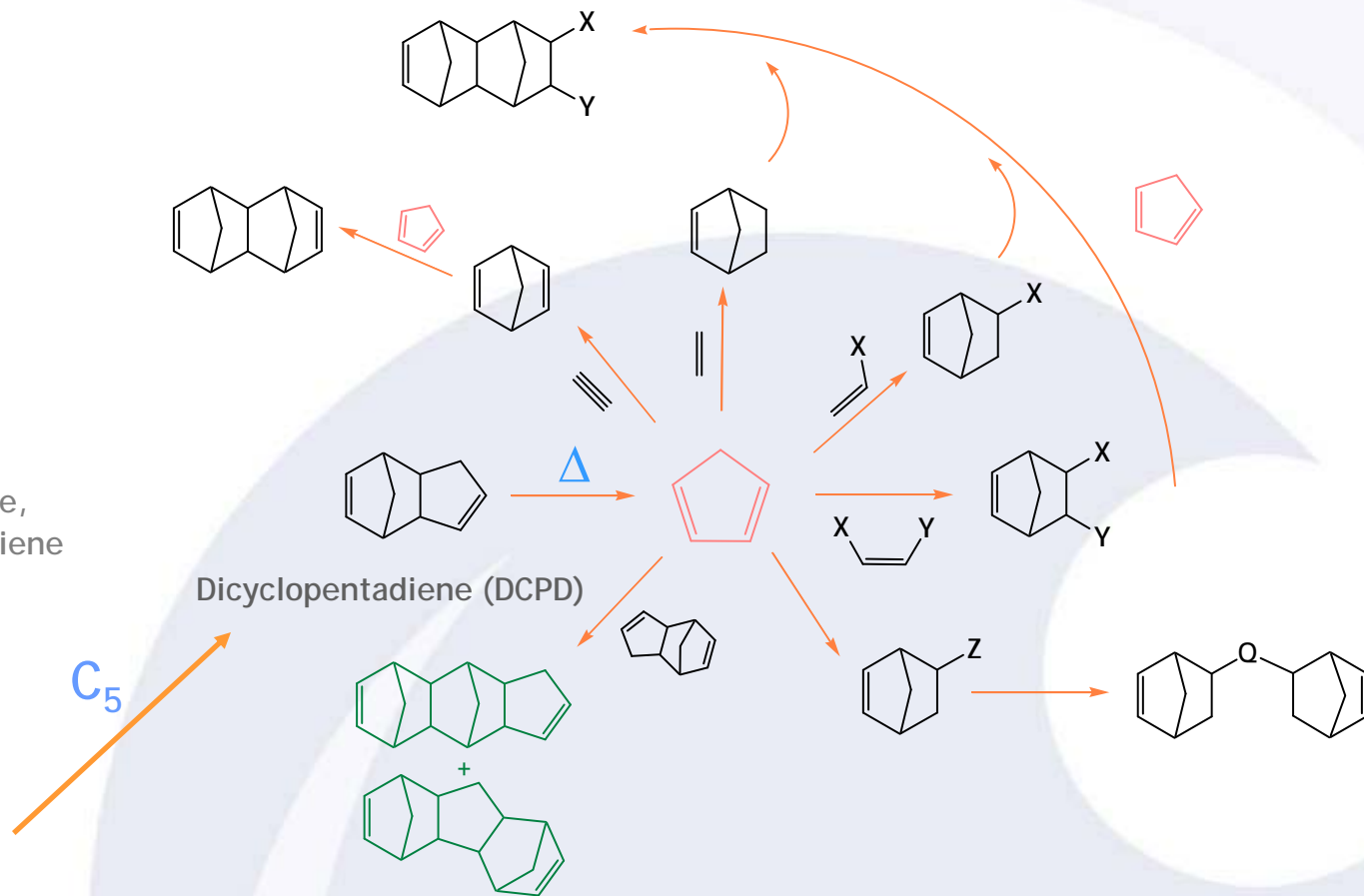
Butane,
Butadiene

C₁

C₂

C₃

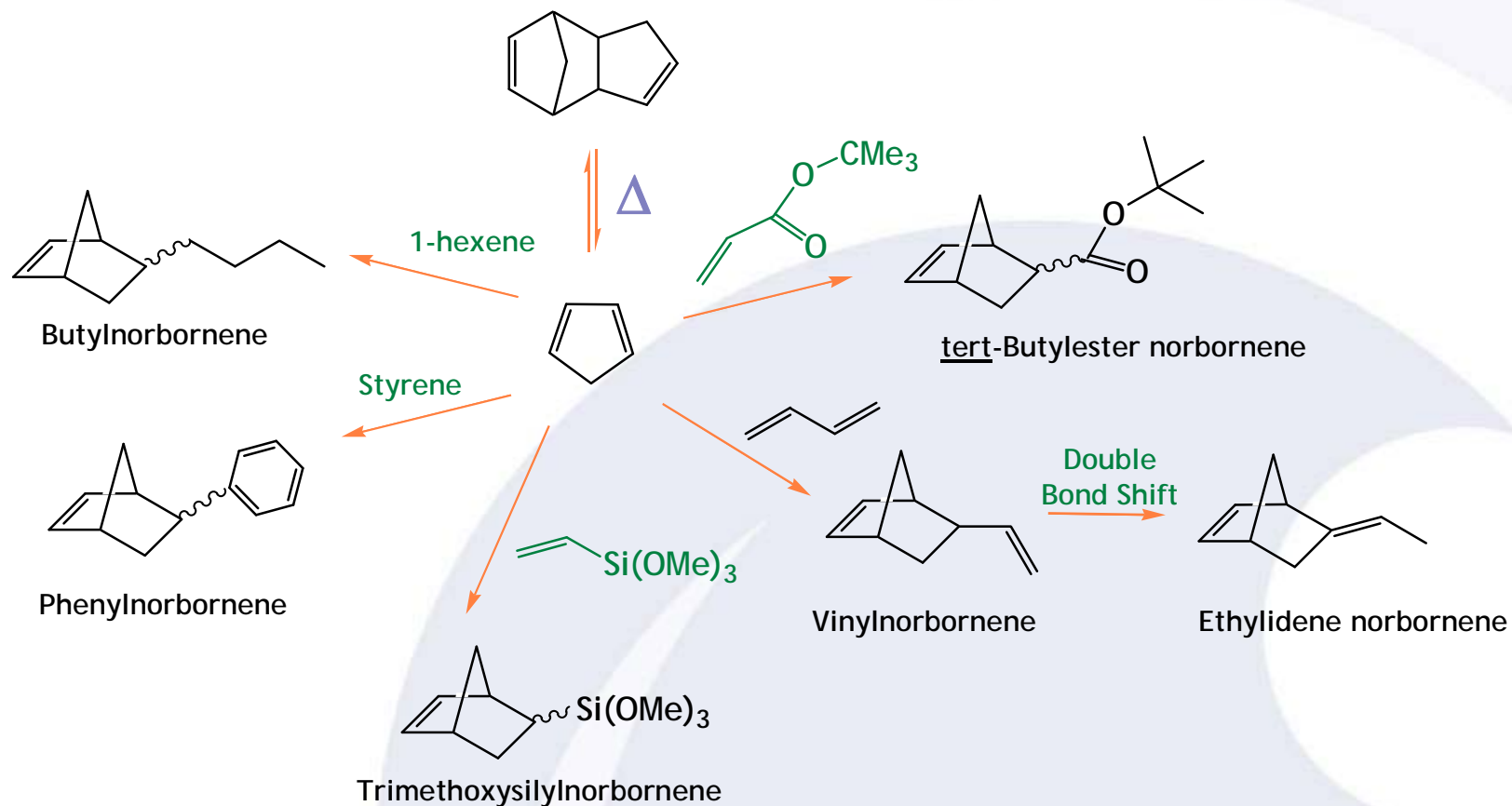
C₄



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Norbornene Derivatives - Examples



One Key to our Success is our Monomers

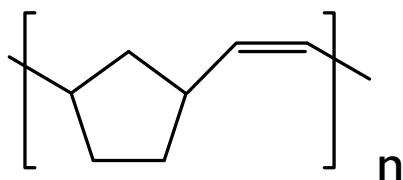
- High Purity
- Ease of Handling
- Multitude of Polycyclic Olefinic Building Blocks
- Huge Variety of Functional Groups
- Crosslinking Monomers
- Ring Strain Drives Polymerization



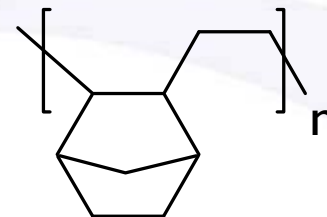
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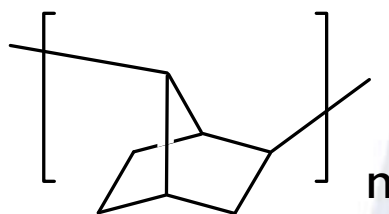
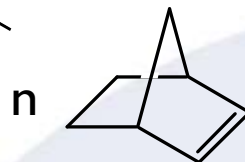
How is Norbornene Polymerized?



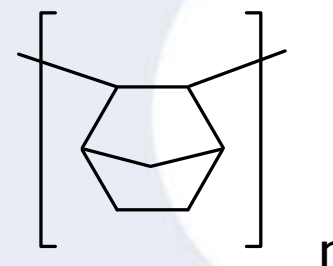
Ring-Opening
Metathesis
Polymerization
(ROMP)



Ethylene Norbornene
Co-Polymerization



Radical or Cationic



Vinyl- or Addition-
Polymerization



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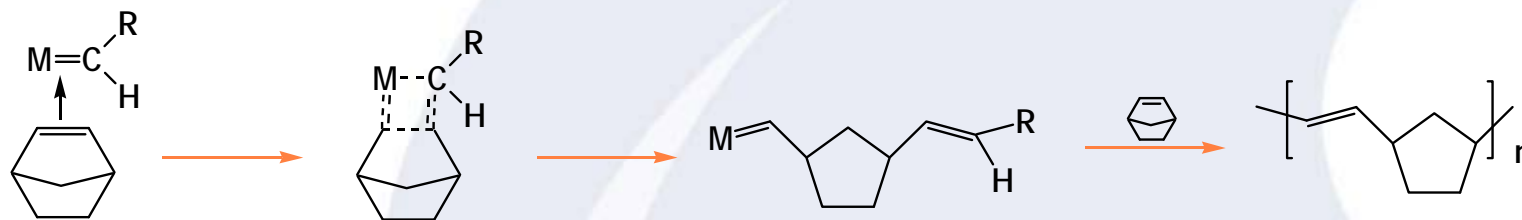
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AP and ROMP Catalysts Yield Different Polymers

Addition Polymerization (AP) - Saturated



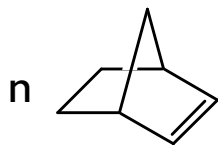
Ring-Opening Metathesis Polymerization (ROMP) - Unsaturated



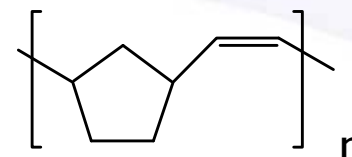
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Several Transition Metal Initiators Can Be Used to Polymerize Norbornene

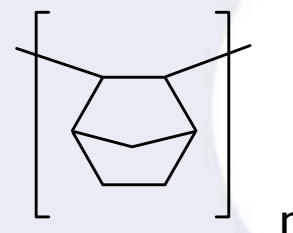


Ti, Ta, Mo, W,
Re, Ru, Os, Ir, Co



Ring-Opening
Metathesis
Polymerization
(ROMP)

Ti, Zr, Cr,
Co, Ni, Pd



Vinyl-Addition

Predominant Transition Metals Employed in Bold



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Our Catalysts have Many Benefits

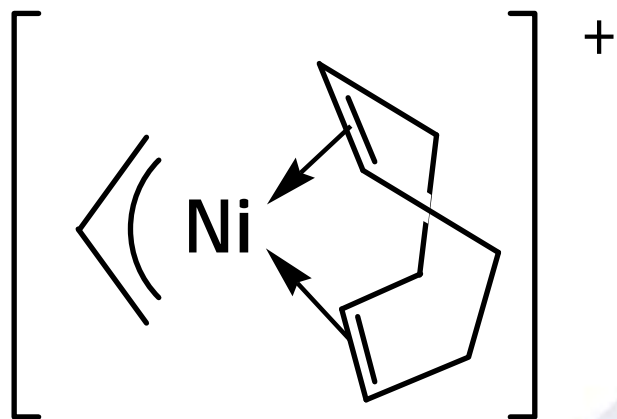
- High Activity, Single Component
- Low Residue in Purified Polymer
- Well-controlled Molecular Weight
- Functional Group Tolerance, e.g.,
 - ✓ Alkyl
 - ✓ Aryl
 - ✓ Ester
 - ✓ Epoxide
 - ✓ Ether
 - ✓ Silyl ether
 - ✓ Carboxylic Acid
 - ✓ Alcohol



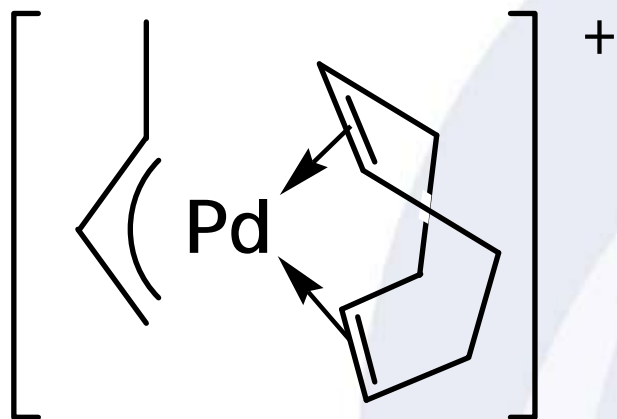
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Some of our Catalysts are Well-defined Initiator Cationic Species



- Hydrocarbyl (or Hydride) Initiating Site
- “Naked” Cationic Metal Center
- Nickel and Palladium are Most Active



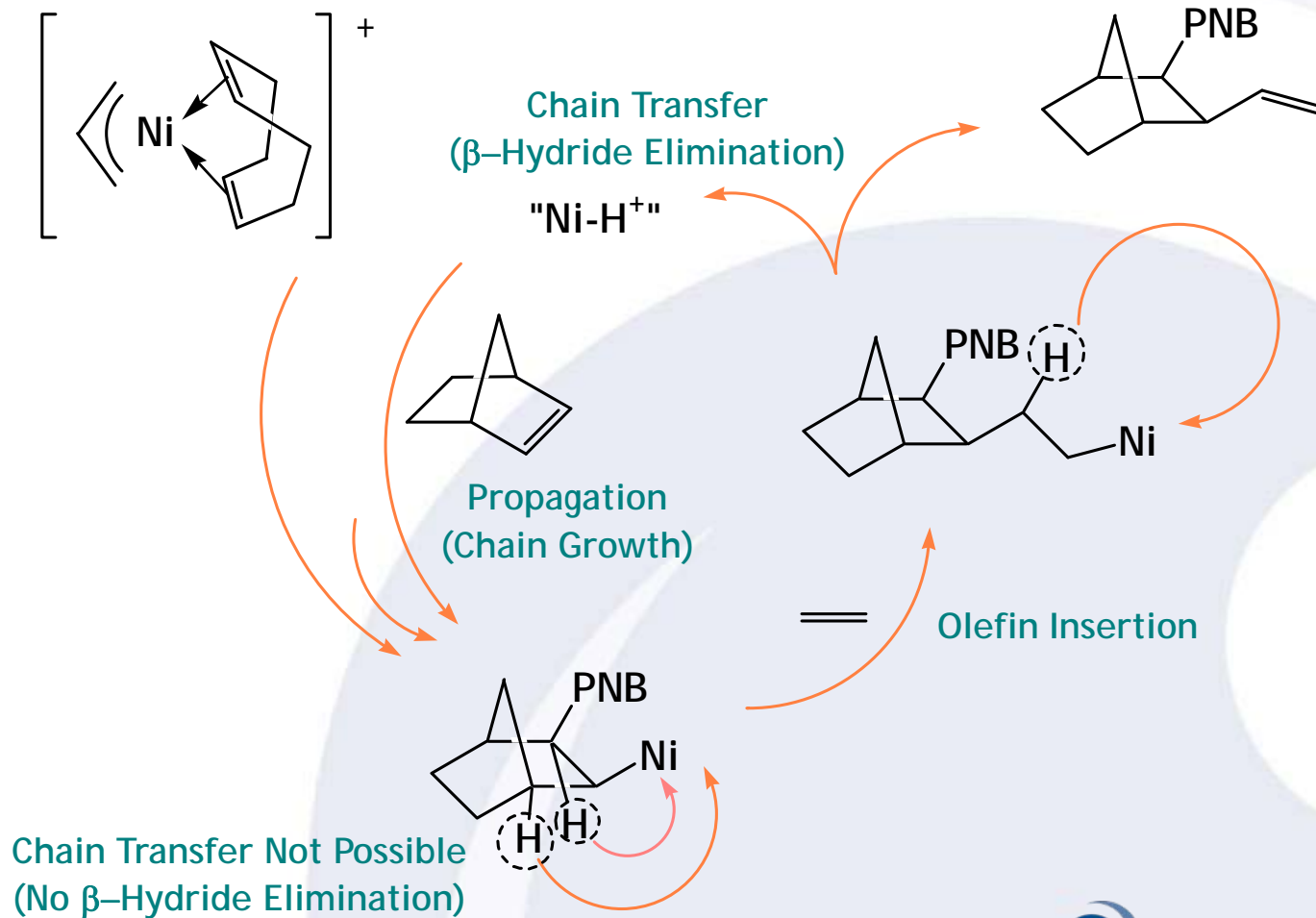
- Weakly Coordinating Anion
 - ✓ BF_4^-
 - ✓ PF_6^-
 - ✓ $\text{B}(\text{C}_6\text{F}_5)_4^-$



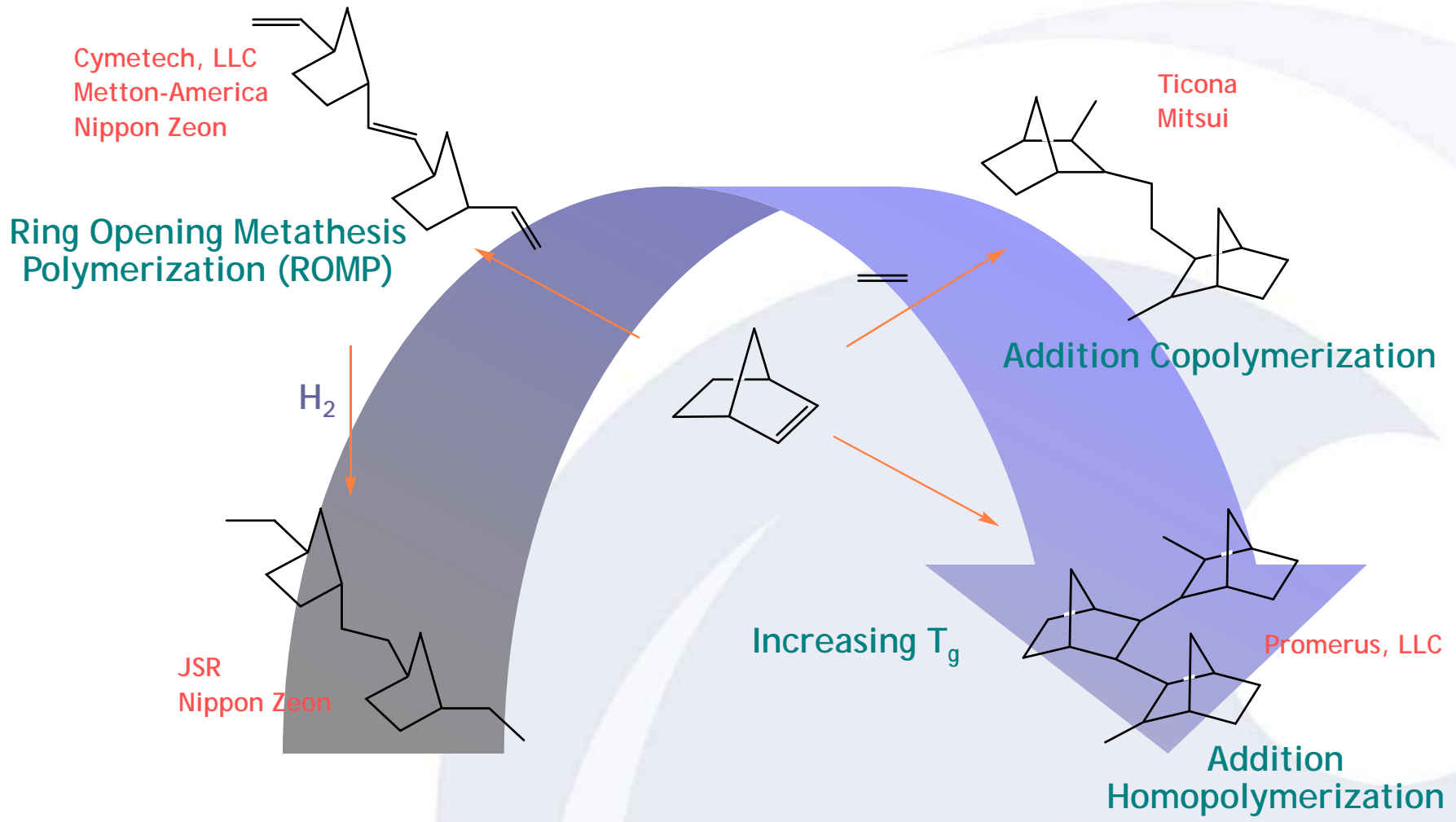
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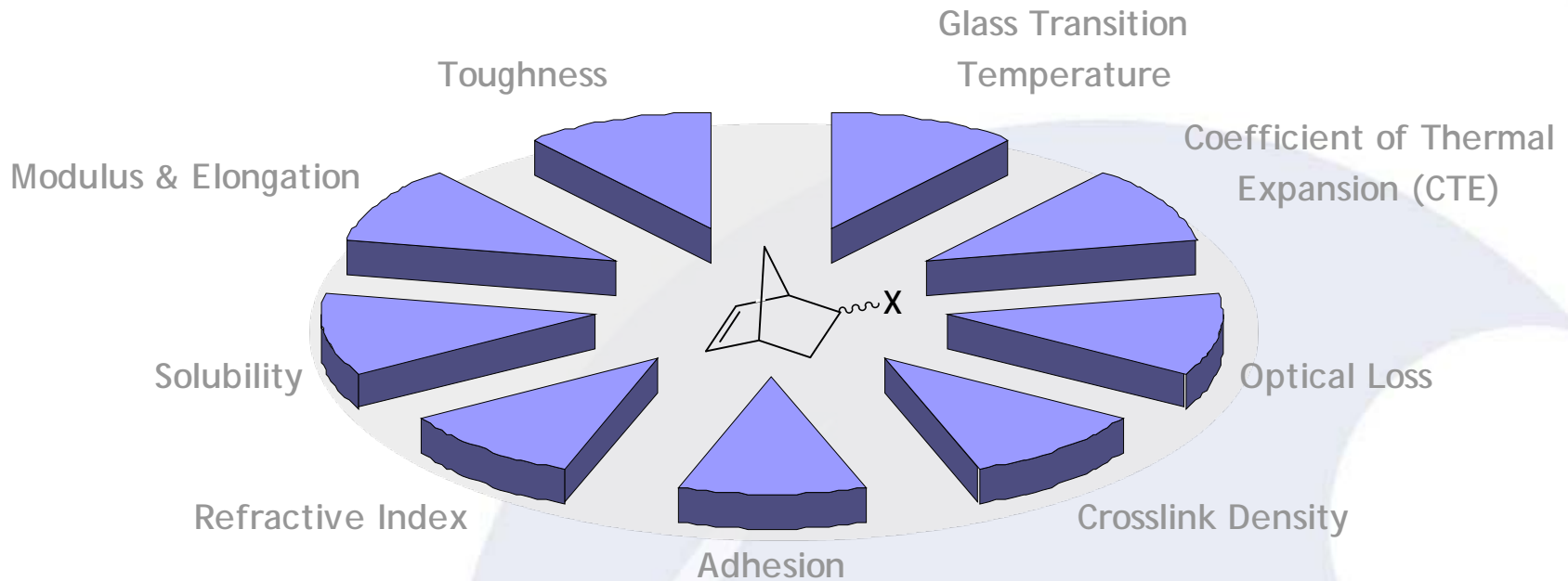
We Can Achieve Molecular Weight Control Via Chain Transfer



Promerus Polymers Have High T_g



Polymer Properties Are Controlled by Changing the Functional Group



Why Use Promerus Polycyclic Olefin Polymers?

Amorphous Polyolefin

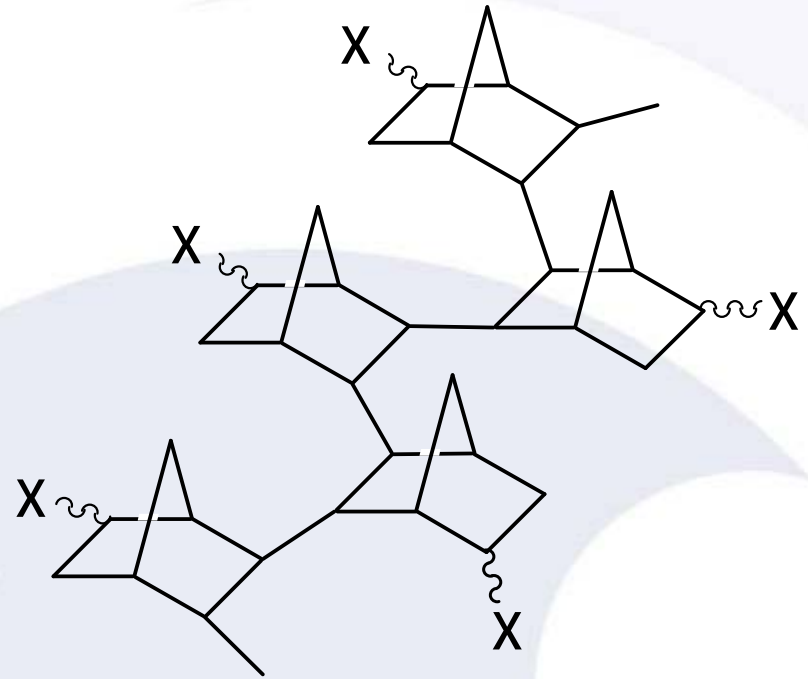
- Wide Spectral Window
- Low Moisture Absorption
- Low Dielectric Constant
- Chemical Resistance
- Low Birefringence
- Low Dielectric Loss
- High Breakdown Voltage

Rigid Polycyclic Backbone

- High T_g

Tailoring Polymer via Functional Group (X)

- Adhesion
- Refractive Index
- Latent Reactivity



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Promerus Materials Can Be Processed in Many Ways

Solution

- Spin Coating
- Solvent Casting

Post Treatment

- Photodefinable
- Latent Crosslinking
- Thermal Decomposition
- Surface Property Enhancement

Mass Polymerization

- Casting
- Resin Transfer Molding (RTM)
- Reaction Injection Molding (RIM)
- Screen-Printing
- Thixotropic Materials
- Composites



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Promerus Materials Are Useful in Many Applications

- Avatrel[®] Dielectric Polymers
 - ✓ For Electronic Packaging and Redistribution Layers
- Unity[®] Sacrificial Materials
 - ✓ For MEMS WLP, Protective Coatings and Temporary Wafer Bonding
- DUVCOR[™] Photoresist Polymers
- Appear[™] Optical Polymers
- Enestra[®] Optical Encapsulant
- Aprima[®] Adhesives



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