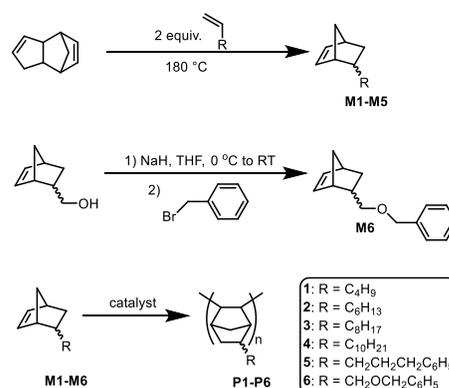


- Grant #: 59132
- Title: Melt Processable Vinyl-Added Polynorbornenes for Advanced Thermoplastics
- PI: Gila Stein, University of Tennessee
- co-PI: Brian Long, University of Tennessee

**Overview:** The synthesis of polynorbornenes via vinyl-addition polymerization produces polymers with high glass transition temperatures, as well as high thermal and oxidative stability. However, these materials often decompose near their glass transition temperatures, and their nonpolar structure can prevent their integration into multi-component systems. To address these issues, the objective of this research program is to synthesize vinyl-addition polynorbornene derivatives (VA-PNBs) that are glassy at elevated temperatures, melt processable, and that incorporate polar substituents to tune adhesion, wetting, surface energy, and blend compatibility. Our approach is based on the copolymerization of substituted norbornene monomers: as examples, flexible hydrocarbon moieties will be used to depress glass transition temperatures and enable melt processing, while aromatic or polar groups are incorporated to tune interactions at surfaces and interfaces. To efficiently explore a large parameter space that includes ca. 100 binary monomer combinations spanning a range of compositions, we are implementing a systematic approach in which we use measurements of homopolymer properties to estimate the thermal stability and melt processability of copolymers. The most promising of the “estimated” designs are then synthesized and characterized to validate the approach.

**Results:** Scheme 1 summarizes the chemistries we have explored in Year One of this award. Monomers **M1-M4** have linear alkyl substituents of increasing length. Monomers **M5** and **M6** have phenylpropyl and benzyloxymethyl substituents, respectively. Monomers **M1-M5** were synthesized via Diels-Alder reaction of cyclopentadiene, which was generated in situ from the cracking of dicyclopentadiene, and the corresponding alkene. Monomer **M6** was synthesized via Williamson ether synthesis of 5-norbornene-2-methanol and benzyl bromide. All monomers were homopolymerized using the catalyst  $(\eta^3\text{-allyl})\text{Pd}(\text{i-Pr}_3\text{P})\text{Cl}$  and were activated using  $\text{LiBAR}^{\text{F}}$  ( $\text{BAR}^{\text{F}} = \text{B}(\text{C}_6\text{F}_5)_4$ ). Polymerizations of **M1-M5** proceeded in high yield (> 80%) to produce polymers **P1-P5** and achieved molecular weights near the theoretical limit. In contrast, polymerization of monomer **M6** proceeded in lower overall yield (60%) and reduced molecular weights for polymer **P6**. This effect is likely associated with interactions between the polar substituent and the catalyst. All students conducting synthesis received safety training from the Department of Chemistry’s departmental safety officer prior to starting this work. Furthermore, standard operating procedures were discussed for all aspects of this work, including the use of flammable reagents and solvents, high temperature and high-pressure reactors/vessels, and hazardous waste handling and disposal.



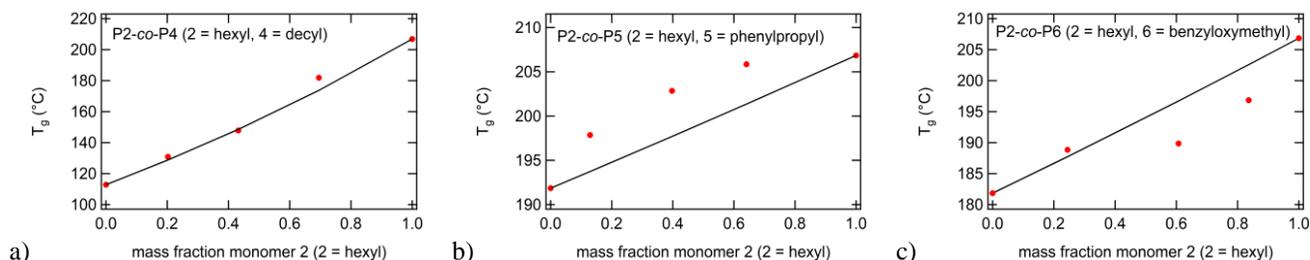
**Scheme 1:** Synthesis of substituted norbornene monomers and of related polynorbornene derivatives.

The melt processability of each homopolymer was evaluated by measuring its glass transition temperature ( $T_g$ ) and decomposition temperature ( $T_d$ ), and then using these data to estimate the “service window”  $T_d - T_g$ . The  $T_g$  was measured by differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and spectroscopic ellipsometry (SE). Each technique yields a different value of  $T_g$ , but the trends are mostly consistent. The  $T_d$  was defined as the temperature at 5% weight loss, and was determined by thermal gravimetric analysis (TGA) with a heating rate of 10 K/min. Table 1 reports the  $T_g$  determined by DMA, the  $T_d$  from TGA, and the service window  $T_d - T_g$ . The measurements of  $T_d$  are still in-progress for homopolymers **P3-P5**. However, of the materials that are fully characterized, **P2** shows the most promising thermal characteristics for melt processing: exhibiting a high  $T_d$  of 397 °C and a broad service window of 190 °C.

Homopolymer	$T_g$ (°C)	$T_d$ (°C)	$T_d - T_g$ (°C)
<b>P1</b>	277	397	119
<b>P2</b>	207	397	190
<b>P3</b>	192	IP	IP
<b>P4</b>	113	IP	IP
<b>P5</b>	192	IP	IP
<b>P6</b>	183	329	146

**Table 1:** Glass transition temperature ( $T_g$ ) from DMA, decomposition temperature ( $T_d$ ), and service window ( $T_d - T_g$ ) of polynorbornene homopolymers **P1-P6**. IP = in progress.

Finally, a series of copolymers based on monomer **M2** with comonomers **M4**, **M5** or **M6** were also synthesized. These materials were synthesized to compare estimated and measured copolymer properties. As an example, Figure 1 shows the  $T_g$  from DMA as a function of monomer composition for each material. The measurements are compared to predictions made using the Fox equation. In material **P2-co-P4**, which is a copolymer of two alkyl-substituted monomers, the measured  $T_g$  is consistent with this simple model. In materials **P2-co-P5** and **P2-co-P6**, where the distinct substituents have different types of secondary interactions, the measured  $T_g$  shows either positive or negative deviations from the prediction. These deviations are not that large, so the Fox equation is appropriate for a first estimate. However, we are currently working on the synthesis of polymers containing polar functionalities, and we anticipate that this approach may fail with those chemistries. Understanding these limits is one aim of our planned work for Year Two.



**Figure 1:** Measured (symbols) and predicted (line)  $T_g$  of copolymers as a function of monomer **M2** composition. The measured data are from DMA, and the prediction is the Fox equation. a) Copolymer of monomers **M2** and **M4**; b) copolymer of monomers **M2** and **M5**; c) copolymer of monomers **M2** and **M6**.

**Student Impact:** Funding from this project has directly supported the graduate work of Ms. Xinyi Wang. Xinyi is a talented young chemist who is developing a strong skill set with expertise in polymer synthesis and characterization. This project has also included two undergraduate students: Ms. Laura Jeong and Mr. Christopher Love. Laura is a chemical engineering major working on measurements of  $T_g$  using SE, while Christopher was an NSF-REU student who wrote a Python program to fit and analyze these data.

**Impact on Faculty:** Funding from this project has enabled a new direction of research for both the principal and co-investigator that merges their respective expertise in the fields of fundamental polymer science and polymer synthesis. The data acquired from this ND seed grant will be used in future grant applications to federal agencies and will be disseminated through forthcoming publications and presentations by both the PIs and students.