

# Effect of pendant groups on fabrication of poly(norbornene imide) single-chain nanoparticles

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## Introduction

Function of biomacromolecules in nature depends largely on their precisely sequenced primary structures and highly tuned tertiary structures. Polymer chemists strive to replicate nature's remarkable ability to fabricate nanomaterials of defined three-dimensional structures. Among these efforts, the intramolecular cross-linking of single linear polymer chain into well-defined globular nano-objects, referred to as single-chain nanoparticles (SCNP), represents a reliable way to synthetically mimic the folding process seen in proteins. (Figure 1)<sup>1</sup>

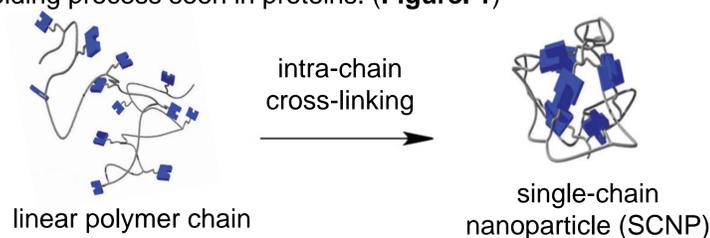
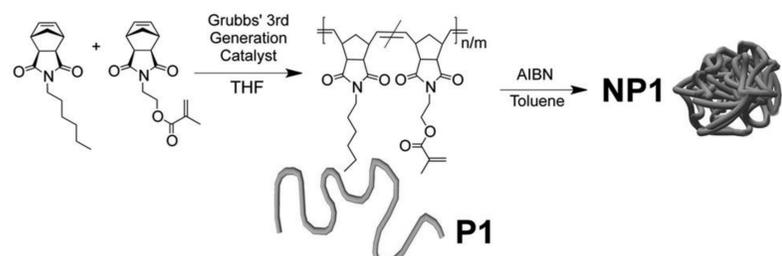


Figure 1: Synthesis of an SCNP from a linear polymer chain

## Previous Work



Scheme 1: Synthetic route to nanoparticle NP1<sup>2</sup>

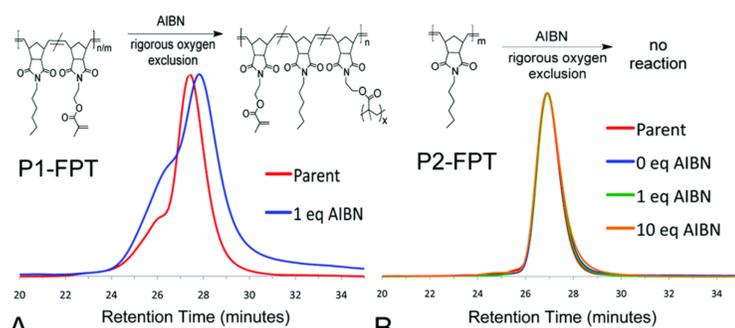
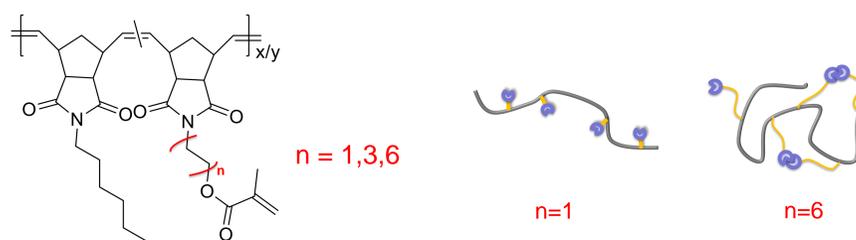


Figure 2: SEC data of exposure of P1(A) and P2(B) to radical crosslinking condition after oxygen exclusion via free-pump-thaw cycles

Poly(norbornene imide) polymers (P1) were collapsed intramolecularly via radical polymerization to yield SCNPs (NP1) (Scheme 1); However, polymer aggregates were also formed via intermolecular crosslinking, leading to the shouldering seen in the SEC data (Figure 2). In order to increase collapse efficiencies, we investigated the collapse dependence on pendant functional groups.

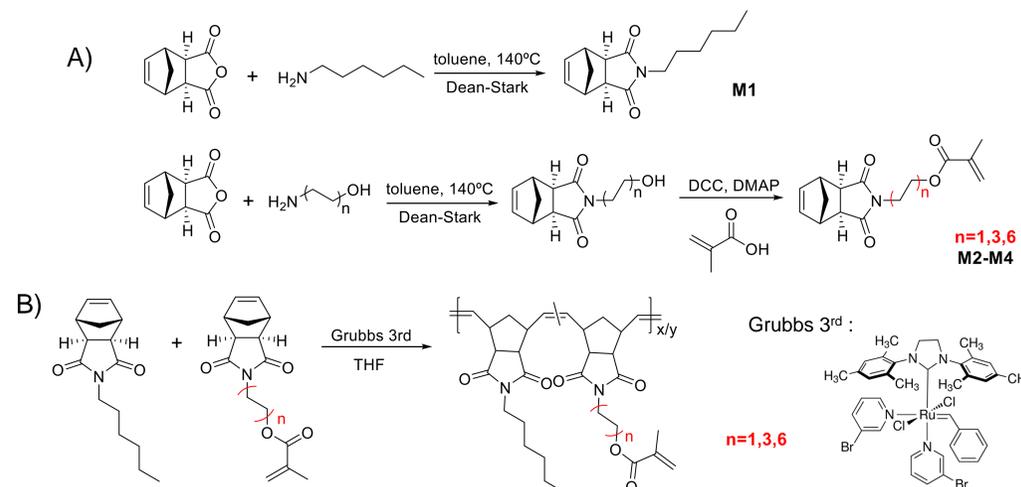
## Polymer Design



Scheme 2: Poly(norbornene imide) polymers with various spacers between polymer backbone and pendant methacryloyl groups

Since the rigid backbone of poly(norbornene imide) prevents movements of the polymer chains and limits possibility of pendant methacryloyl groups to crosslink, we prepared polymers with varying pendant group lengths from the backbone (Scheme 2), and subjected the polymers to intra-chain radical polymerizations in dilute solutions, to study the effect of pendant group length on the efficiency of intramolecular crosslinking.

## Monomer and Polymer Synthesis



Scheme 3: Synthetic route to monomers (A), and poly(norbornene imide) via ring-opening metathesis polymerization (ROMP) (B).

n	Incorp.% methacryloyl groups <sup>a</sup>	Mn <sup>b</sup> (kDa)	Mw <sup>b</sup> (kDa)	D <sup>b</sup>
1	17.7%	46.9	49.2	1.03
3	16.8%	48.2	49.0	1.02
6	13.9%	34.0	34.1	1.01

Table 1: Molecular weight data of synthesized polymers. (a. calculated from <sup>1</sup>H NMR; b. calculated by SEC)

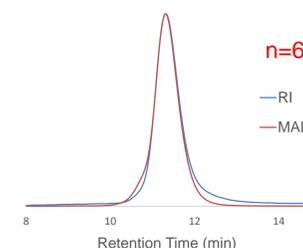
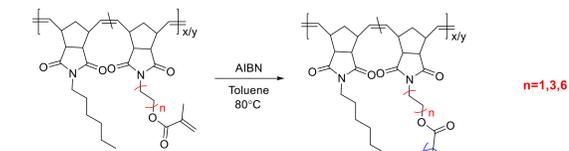
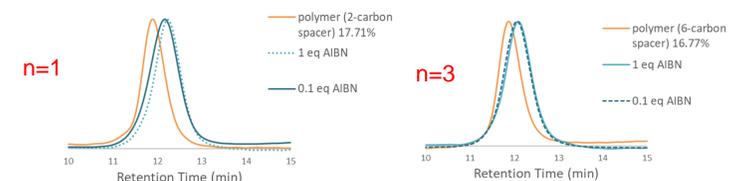


Figure 3: SEC data of poly(norbornene imide) when n=6

## Intra-Chain Radical Polymerization



Scheme 4: Intra-chain radical polymerization of methacryloyl-functionalized poly(norbornene imide) to form SCNPs.



	Rh(v)n (nm)	Intrinsic Viscosity (ml/g)		Rh(v)n (nm)	Intrinsic Viscosity (ml/g)
Polymer(n=1)	6.9	44.2	Polymer(n=3)	7.0	45.0
0.1 eq AIBN	5.5	20.3	0.1 eq AIBN	6.0	25.5
1 eq AIBN	5.4	16.2	1 eq AIBN	5.7	21.1

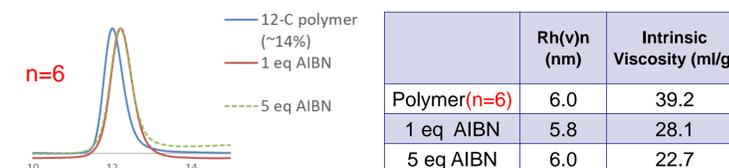


Figure 4: Intra-chain cross-linking experiments on poly(norbornene imide) to form SCNPs.

## Summary and Future Work

We successfully fabricated poly(norbornene imide) SCNPs via intra-chain radical polymerization, and studied the effect of pendant groups on the synthesis of these SCNPs. Current result showed little correlation between the pendant group lengths and collapse efficiency of the polymers. Future work will be to focus on changing percent incorporations of the methacryloyl-functionalized monomers in the copolymerization, and to further investigate collapse dependence on pendant groups.

## Acknowledgements

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## References

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- Cole, J. P.; Lessard, J. J.; Lyon, C. K.; Tuten, B. T.; Berda, E. B., Intra-chain radical chemistry as a route to poly(norbornene imide) single-chain nanoparticles: structural considerations and the role of adventitious oxygen. *Polymer Chemistry* 2015.