

Assessing structure/property relationships and synthetic protocols in the fabrication of poly(oxanorbornene imide) single-chain nanoparticles

Ruiwen Chen, Sarah J. Benware, Justin P. Cole, Jacob J. Lessard and Erik B. Berda. Department of Chemistry, *University of New Hampshire*.



Introduction

Self-folding of single polymer chains in dilute solution create globular nanoparticles, known as single-chain nanoparticles (SCNP).¹ SCNP offers a simplified route to crudely mimic protein tertiary structure, and show promise for applications in catalysis, nanomedicine, sensors, etc.² With the goal of increasing the efficiency of chain folding, we investigated intra-chain radical polymerization as a crosslinking strategy to synthesize SCNP, as it generates no byproduct and offers a possibility to tune the compactness of an SCNP by controlling the degree of intra-chain polymerization (Figure 1).

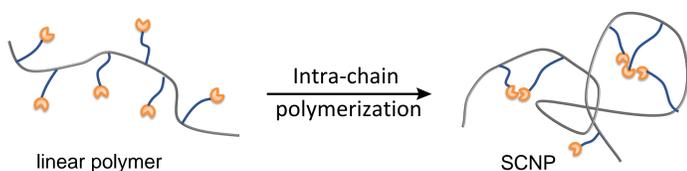
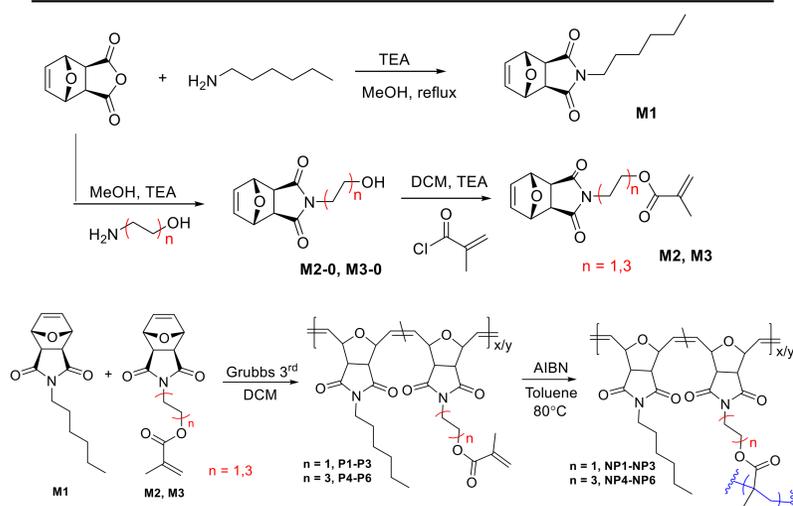


Figure 1: Synthesis of an SCNP from a linear polymer chain.

SCNP Synthesis



Scheme 1: Synthetic route to poly(oxanorbornene imide) SCNP by intra-chain radical polymerization.

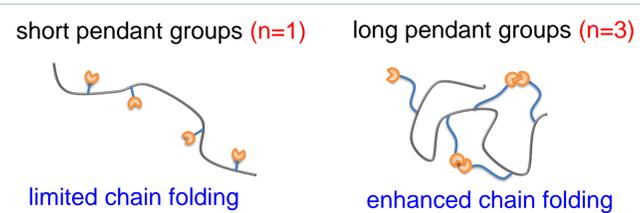


Figure 2: Proposed pendant effect on the efficiency of chain folding.

We surmised it likely that increasing pendant lengths and flexibility will increase the folding efficiency of this semi-rigid polymer chain (Figure 2).

Premature Cross-linking Reaction

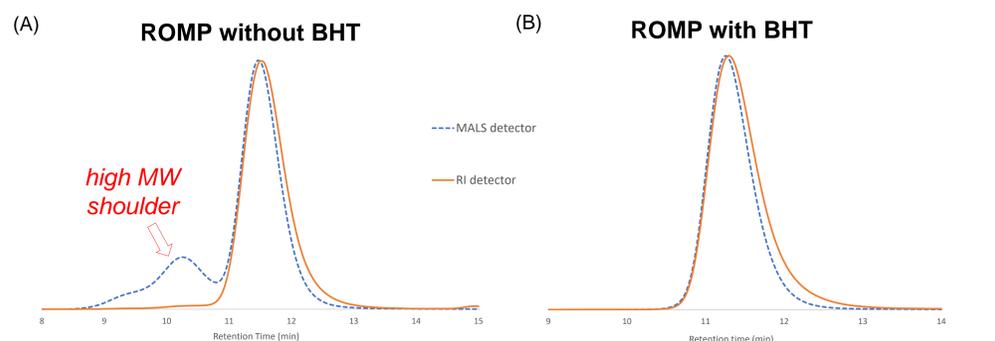
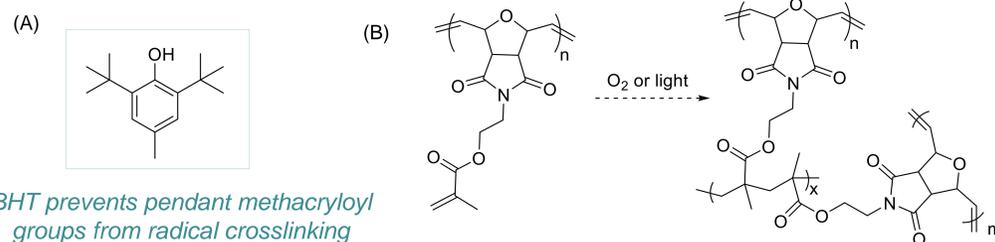


Figure 3: SEC trace of copolymers polymerized (A) without BHT, and (B) with BHT.



BHT prevents pendant methacryloyl groups from radical crosslinking

Scheme 2: (A) Structure of BHT; (B) Possible crosslinking side reaction during ROMP – interchain radical polymerization of pendant groups

Pendant Group Effect

To study structural parameters in relation to chain folding, we initiated intra-chain radical polymerizations on linear copolymers with both short and long pendant groups, and ~10, 20 and 50% incorporations of polymerizable methacryloyl groups. We found that increasing the pendant group length did not noticeably affect the efficiency in folding of a polymer chain at the length scales we synthesized, and the size of the resulting SCNP could be controlled by changing the percent incorporations of pendant polymerizable unit in the parent polymer.

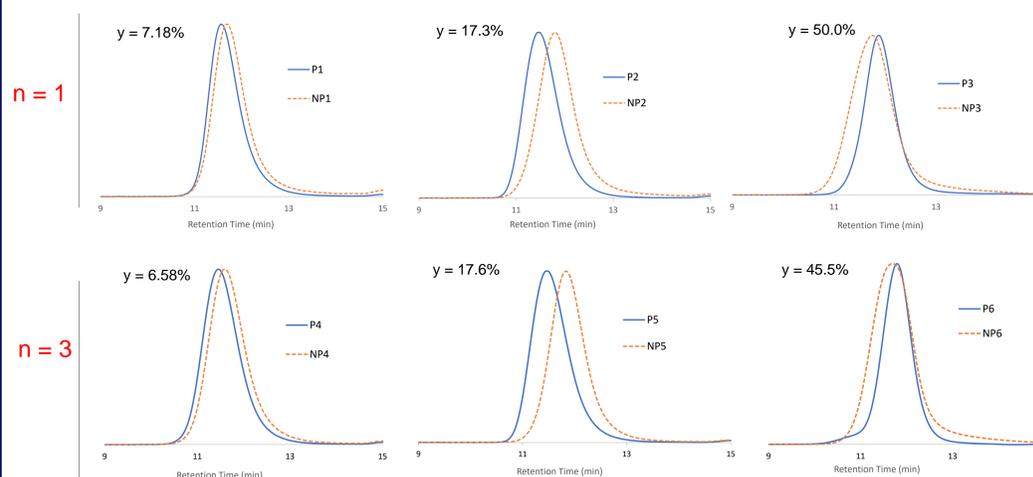


Figure 4: SEC trace of copolymers and corresponding SCNP with short pendant group (n=1) and long pendant group (n=3) with ~10, 20 and 50% incorporation of methacryloyl group.

Copolymerization with Styrene

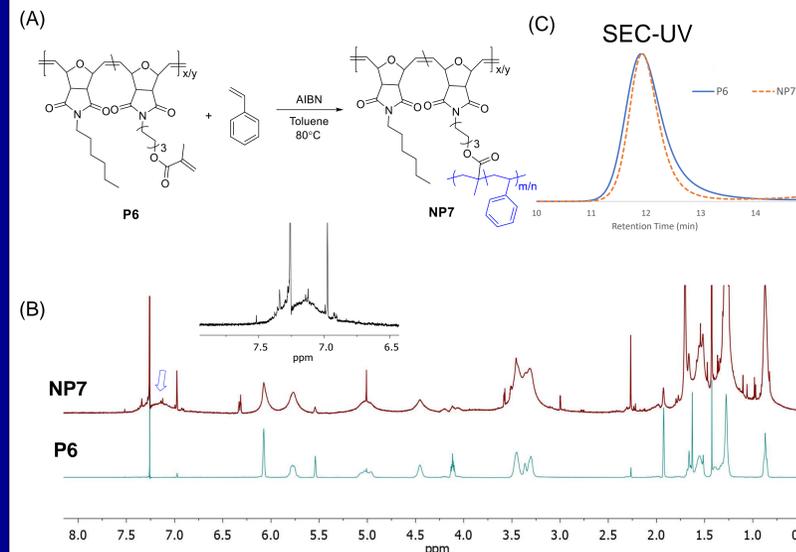


Figure 5: (A) Intra-chain copolymerization of pendant methacryloyl group with styrene; (B) ¹H NMR spectra of P6 and NP7; (C) SEC-UV trace of P6 and NP7.

We added styrene in the intra-chain polymerization of methacryloyl groups. Styrene undergoes copolymerization of pendant groups and with its distinguishable peaks, are easily observed in ¹H NMR (Figure 5).

Summary and Conclusions

We have shown that synthesizing well-defined poly(oxanorbornene imide) in ambient environment through ROMP requires a radical inhibitor to prevent interchain crosslinking. Based on these findings we developed a method for fabricating single-chain nanoparticles through intrachain radical polymerization of pendant methacryloyl groups on poly(oxanorbornene imide). Our results indicate increasing pendant group length did not noticeably affect the efficiency in folding of a polymer chain at the length scales we synthesized. We also demonstrated that by changing the percent incorporations of pendant polymerizable unit in the parent polymer, the size of the resulting nanoparticles could be controlled.

Acknowledgements

The authors would like to graciously thank the Army Research Office for support through award W911NF-14-1-0177 and W911NF-18-1-0216, as well as Drs. Erik Berda, Jon Tsavalas and Marc Boudreau for sharing time and expertise.



References

1. Lyon, C. K.; Prasher, A.; Hanlon, A. M.; Tuten, B. T.; Tooley, C. A.; Frank, P. G.; Berda, E. B., A brief user's guide to single-chain nanoparticles. *Polymer Chemistry* 2015.
2. 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.