

Effect of pendant groups on fabrication of poly(oxanorbornene 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)**¹

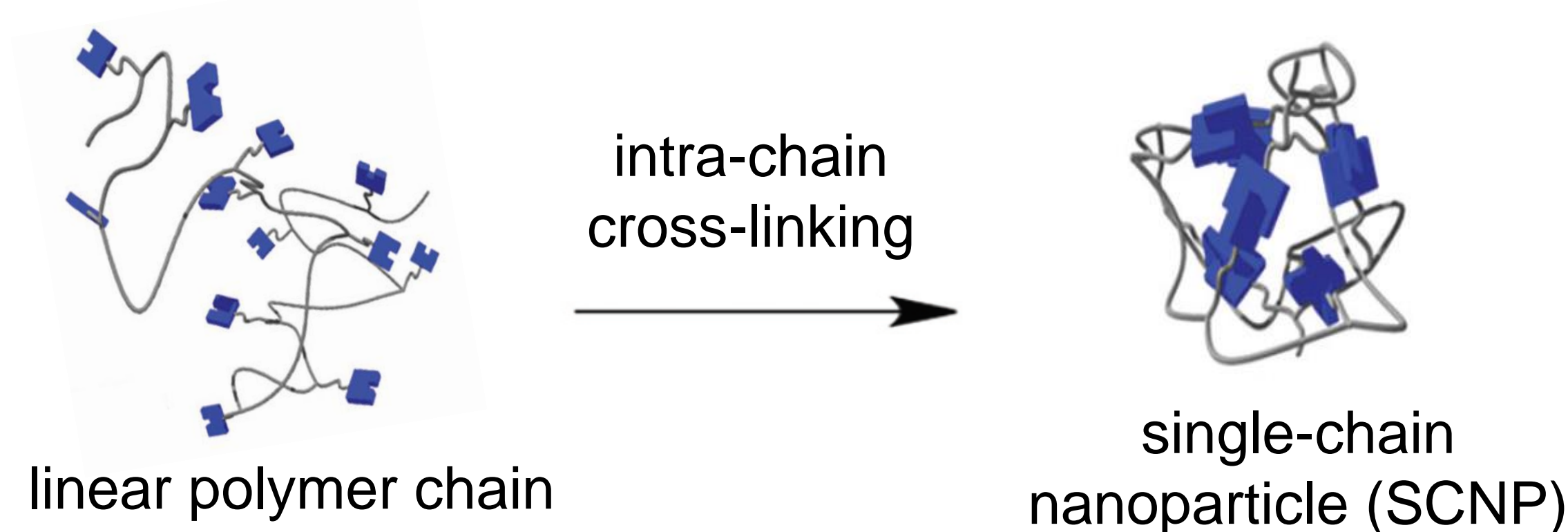
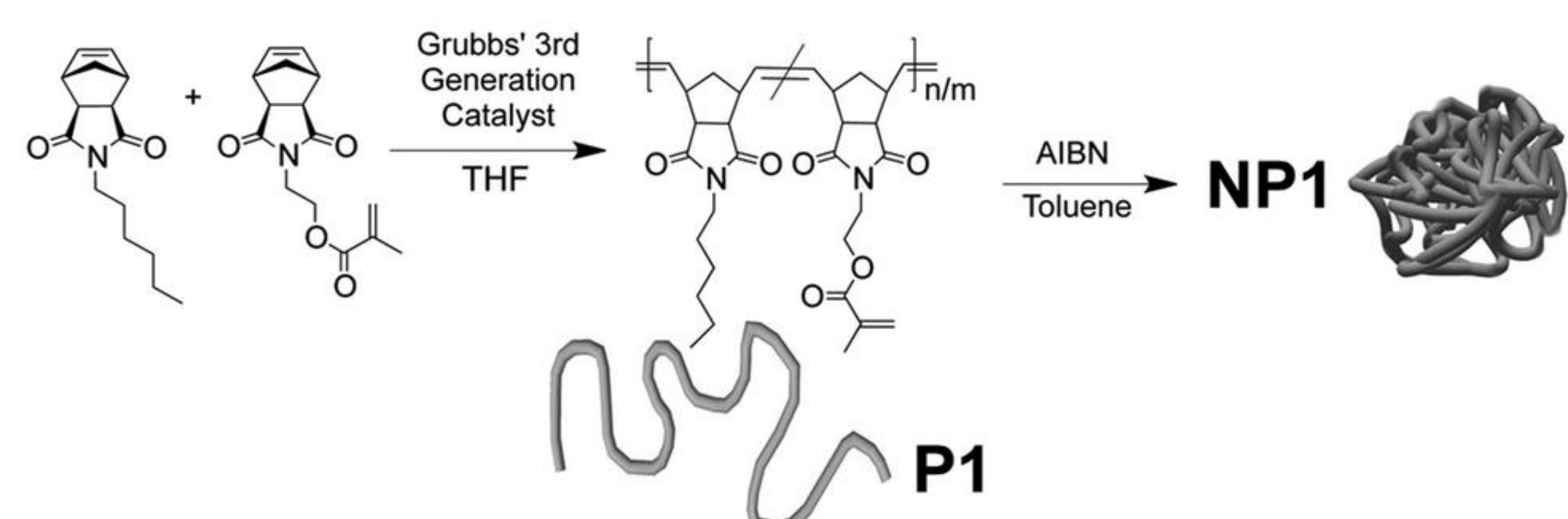


Figure 1: Synthesis of an SCNP from a linear polymer chain

Previous Work



Scheme 1: Synthetic route to nanoparticle NP1²

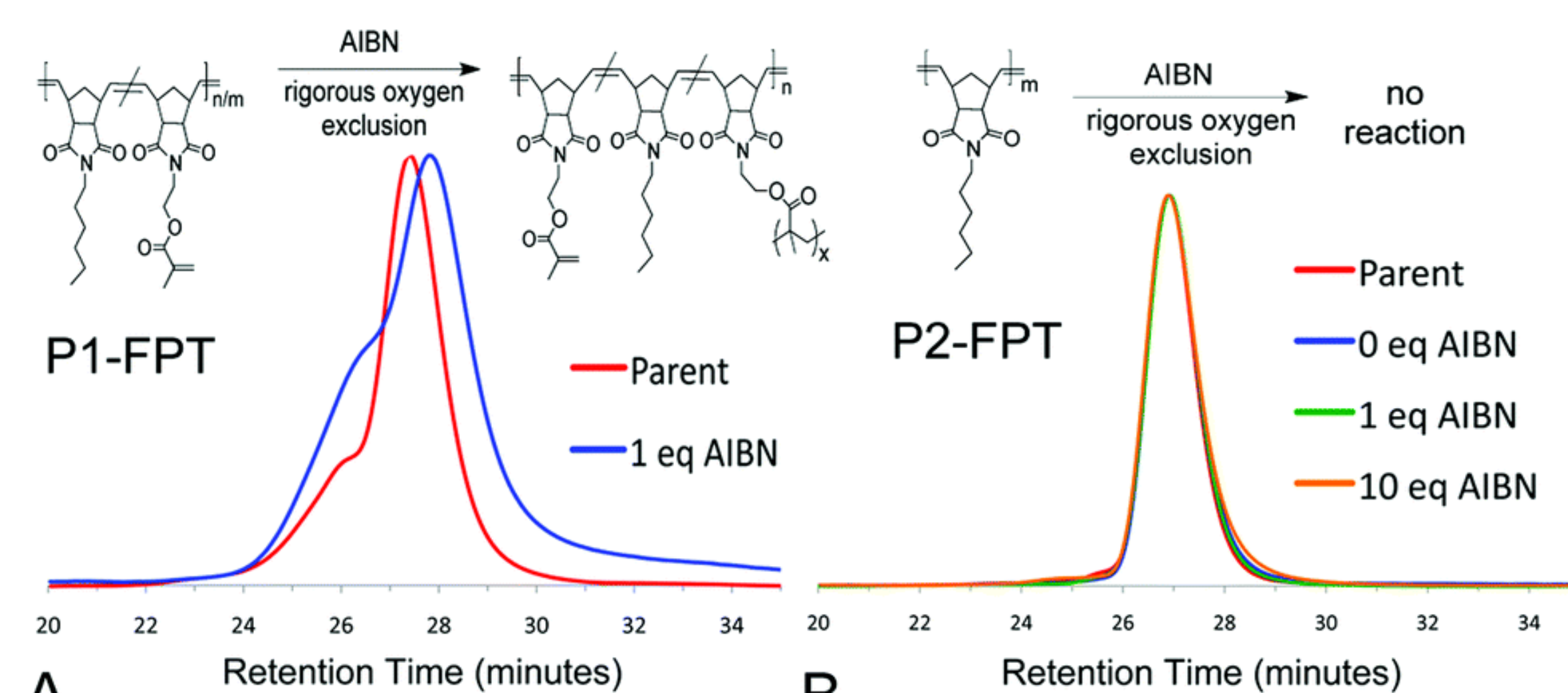
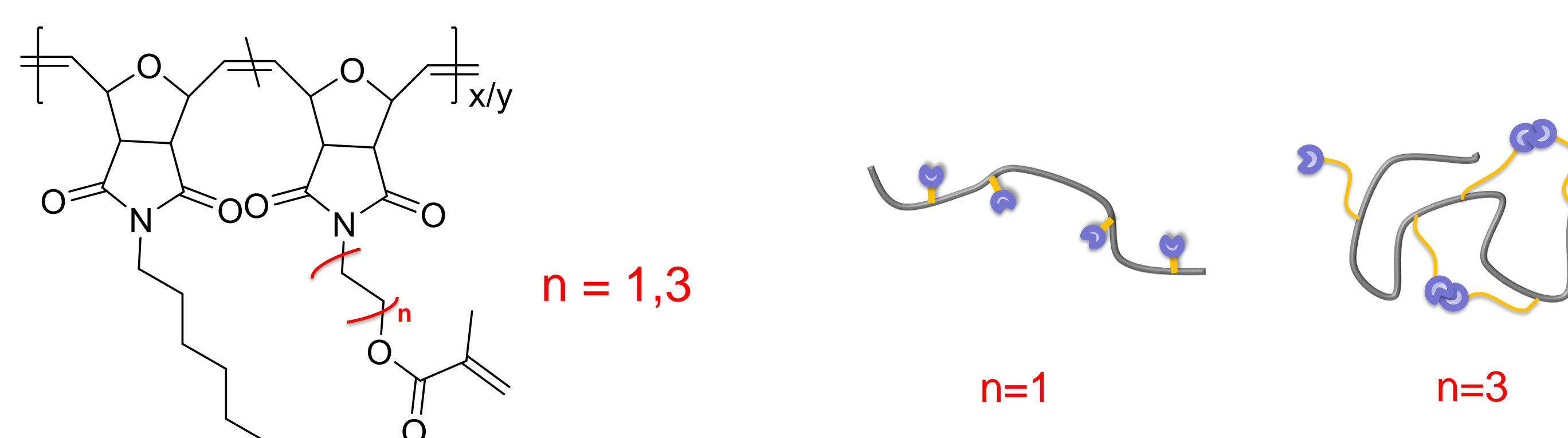


Figure 2: SEC data of exposure of P1(A) and P2(B) to radical crosslinking condition after oxygen exclusion via free-pump-thaw cycles

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)**. To prevent interchain crosslink and increase folding efficiencies, we modified ROMP procedure and investigated the collapse dependence on pendant functional groups.

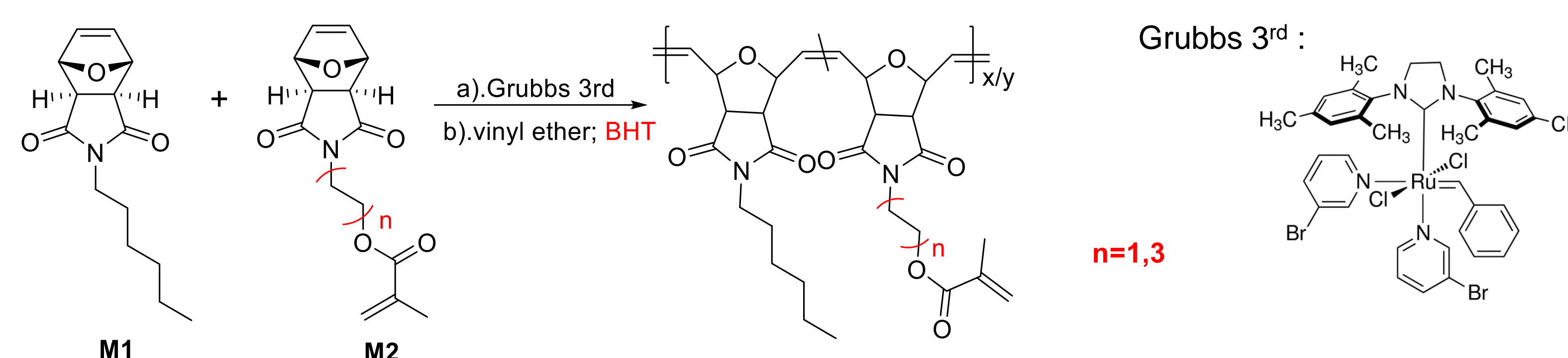
Polymer Design



Scheme 2: Poly(oxanorbornene 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.

Radical Inhibitor's Role in ROMP of M2



Scheme 3: Synthetic route to poly(oxanorbornene imide) via ring-opening metathesis polymerization (ROMP).

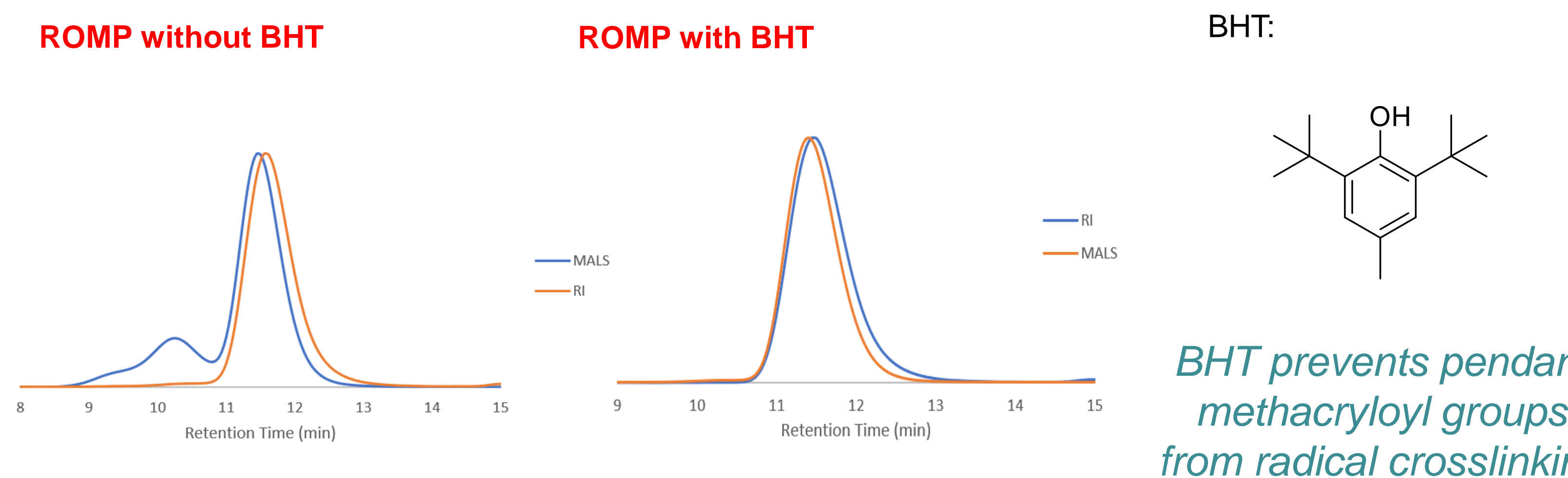
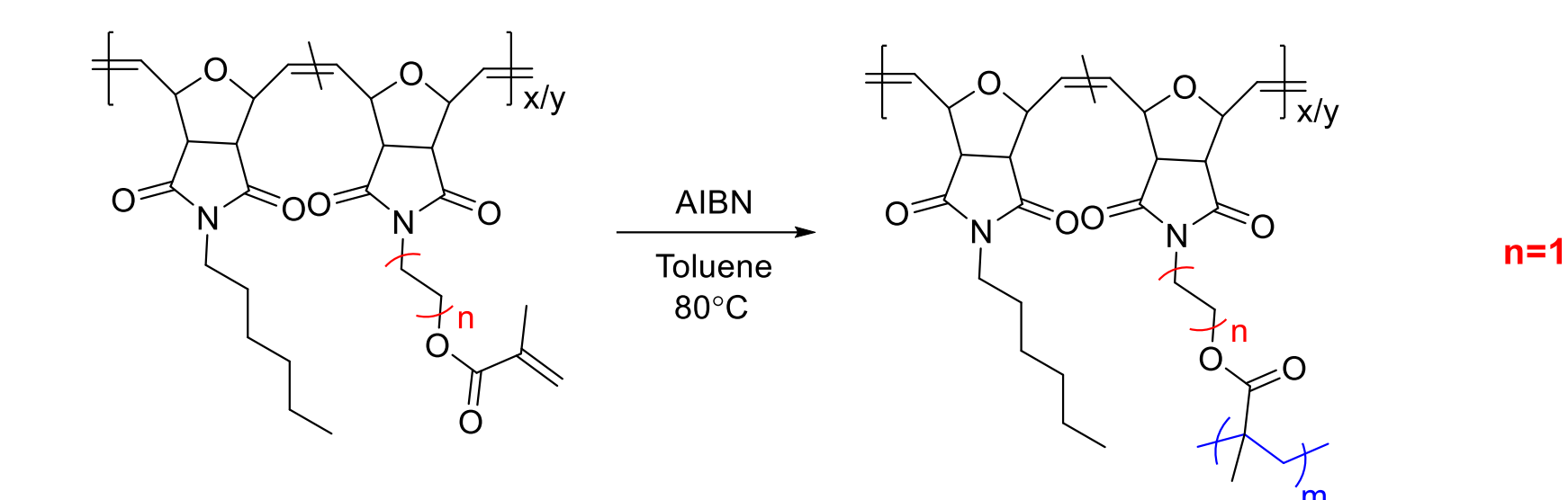


Figure 3: GPC trace of ROMP without (A) and with (B) radical inhibitor BHT.

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

n	Incorp.% methacryloyl groups ^a	M _n ^b (kDa)	M _w ^b (kDa)	Đ ^b	Rh(v)n (nm) ^b	Intrinsic viscosity (ml/g) ^b	dn/dc ^b
1	7.18%	45.5	46.8	1.03	5.40	22.0	0.1162
	17.3%	45.7	47.5	1.04	5.87	29.0	0.1187
3	6.58%	59.4	65.4	1.10	6.09	24.6	0.1187
	17.6%	43.4	45.1	1.04	5.85	30.2	0.1212

Effect of Pendant Groups



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

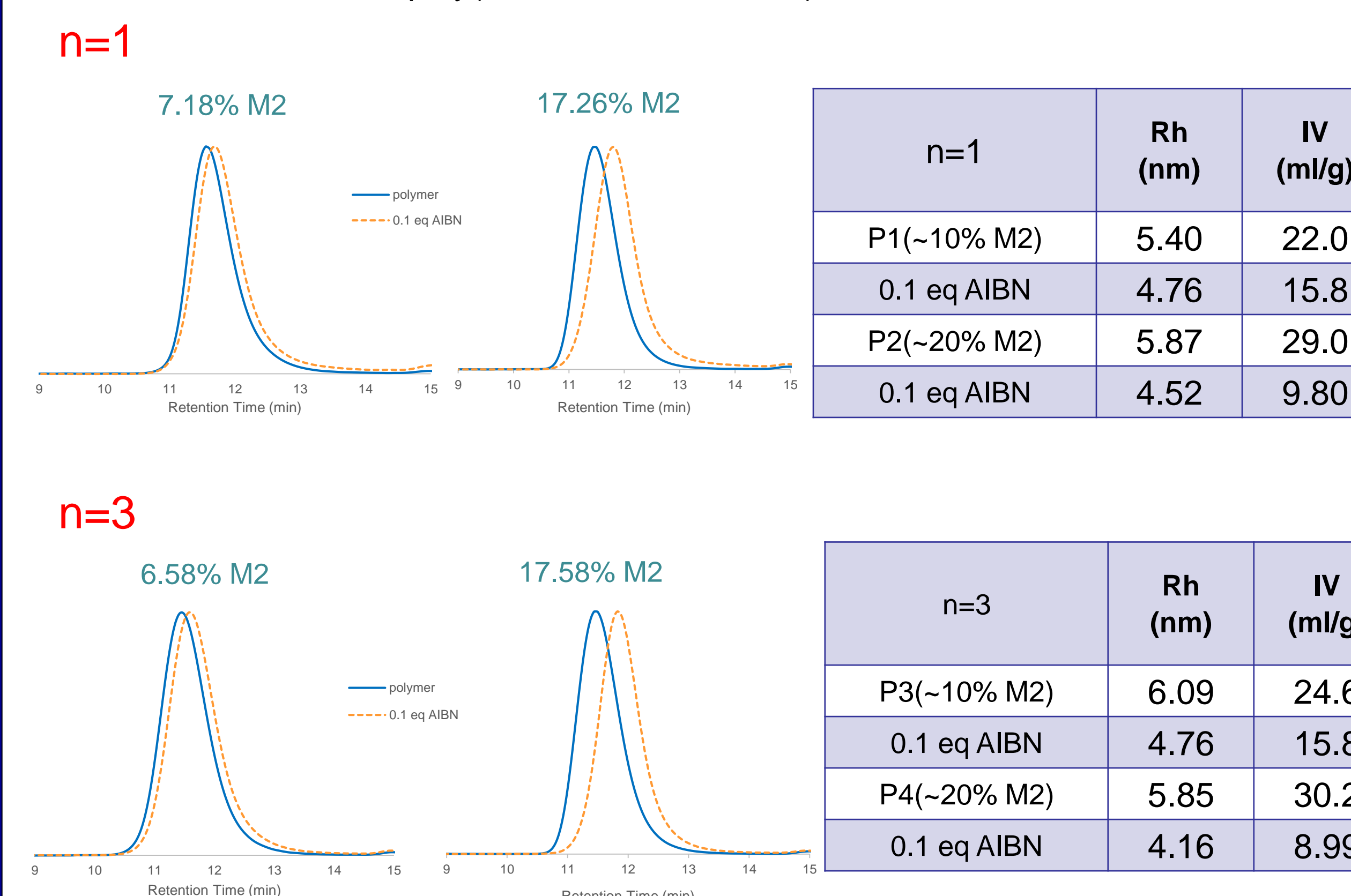


Figure 4: Intra-chain cross-linking experiments on poly(oxanorbornene imide) to form SCNPs.

Summary and Conclusions

We successfully synthesized a series of poly(oxanorbornene imide) with low dispersity by adding a radical inhibitor during ROMP. Subsequent addition of AIBN under dilute condition result in folding of single polymer chains yielding SCNPs. We studied the effect of pendant groups on fabrication of SCNPs. Current result showed little correlation between the pendant group lengths and collapse efficiency of the polymers. However, percent incorporation of methacryloyl groups were found to have a profound effect on folding of single polymer chains.

Acknowledgements

The author 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**.