Controllable Synthesis of SCNPs *via* ATRC

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Introduction

New macromolecules with complex and diversely functionalized architectures are thought to have a promising future in applications such as drug delivery and catalysis by means of mimicking protein-like structures.[1,2] The synthesis of such macromolecules brings forth many desirable architectural and functional capabilities such as the control of architecture, size, and functionality.[3] Our research has employed a combination of controlled radical polymerizations and efficient cross-linking chemistries to prepare and characterize single-chain nanoparticles (SCNPs).

Experimental Design

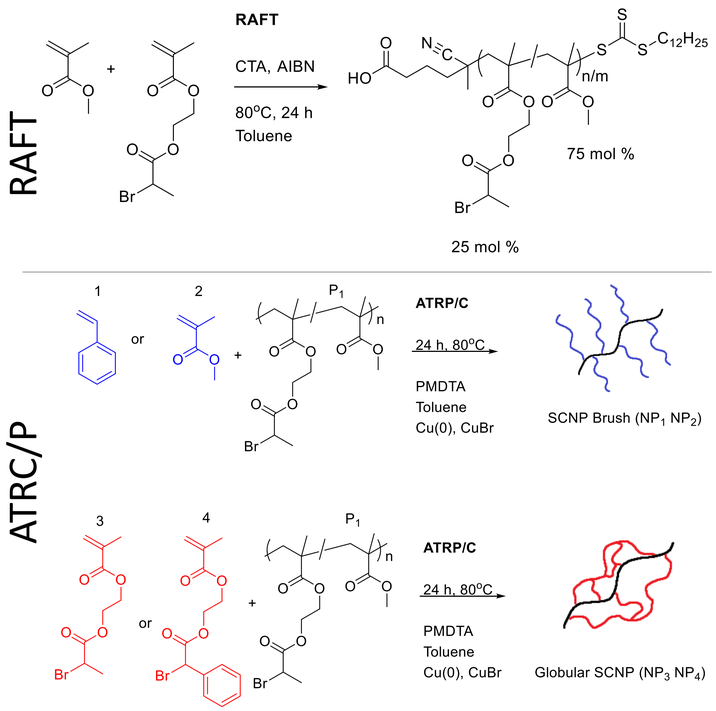

Figure 1: Overview of architecture oriented SCNP synthesis.

Structural verification *via* nuclear magnetic resonance spectroscopy (NMR) and molecular weight data *via* gel permeation chromatography (GPC).

Results and Discussion

Resulting NMR spectra and GPC data indicated success in morphological and functional control.

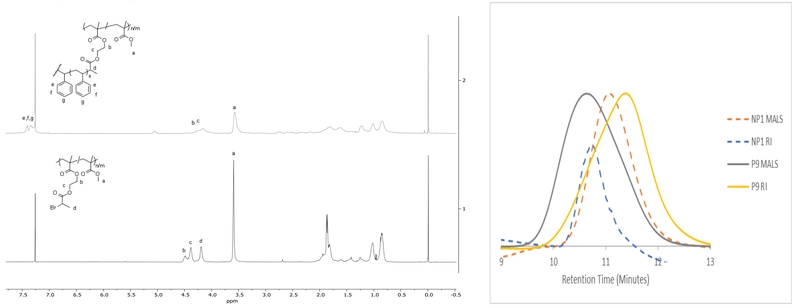

Figure 2: NMR (left) and GPC trace (right) of NP_1 and Parent

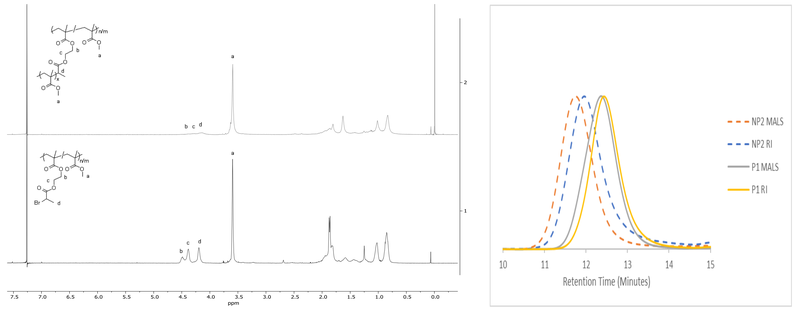

Figure 3: NMR (left) and GPC trace (right) of NP_2 and Parent

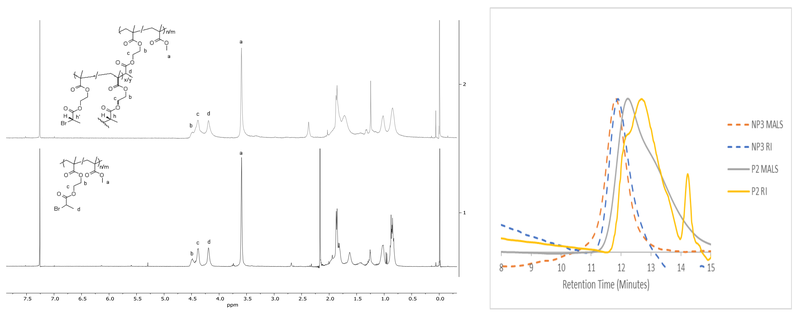

Figure 4: NMR (left) and GPC trace (right) of NP_3 and Parent

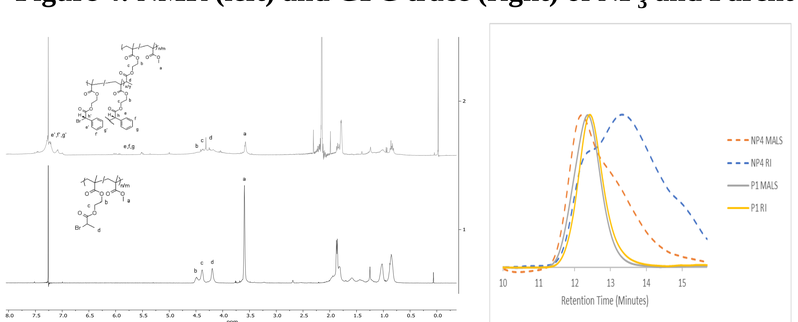

Figure 5: NMR (left) and GPC trace (right) of NP_4 and Parent

Sample	Parent (NP) or F (P)	Mw (g/mol)	Mn (g/mol)	Đ	$Rh(V)_n$	$[n]_n$
Styrene Brush (NP_1)	P_9	2.358E+5	1.627E+5	1.449	6.272	10.901
MMA Brush (NP_2)	P_1	5.136E+4	3.671E+4	1.399	3.748	9.492
MeBrema Hypergraft (NP_3)	P_2	2.089E+5	1.943E+5	1.075	4.002	2.128
PhBrema Hypergraft (NP_4)	P_1	3.929E+5	1.334E+5	2.944	6.730	20.060
p(MMA)-co-(MeBrema) (P_1)	31.7	6.756E+3	5.916E+3	1.142	2.379	12.811
p(MMA)-co-(MeBrema) (P_2)	35.7	1.189E+4	7.901E+3	1.186	1.603	3.201
p(MMA)-co-(MeBrema) (P_9)	37.9	9.629E+4	5.686E+4	1.694	4.736	13.473

Figure 6: GPC morphological data of NPs and Parents

Styrene's ability to undergo ATRC resulted in aggregation, yielding unfavorable MALS traces. MeBrema incorporation is also presumed to have resulted in aggregation, giving similar results.

Future Work

Aggregation in select SCNP formation proved to be an aspect lacking in control – further synthetic design needed.

Conclusions

-Parent polymer (P_n) synthesis conducted without issue
-Comonomer incorporation was successful
-Morphology of SCNPs controlled with limitations
-Aggregation proven to hinder evaluation of morphology

Acknowledgements

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References

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2) Perez-Baena, I.; Barroso-Bujans, F.; Gasser, U.; Arbe, A.; Moreno, A. J.; Colmenero, J.; Pomposo, J. A. ACS Macro Lett. 2013, 2(9) , 775-779.
3) 3) Lu, Y.; Nemoto, T.; Tosaka, M.; Yamago, S.; Nature Communications, 2017, 8, 1863