Single-chain nanoparticles *via* coupling product of intra-chain atom transfer radical polymerization

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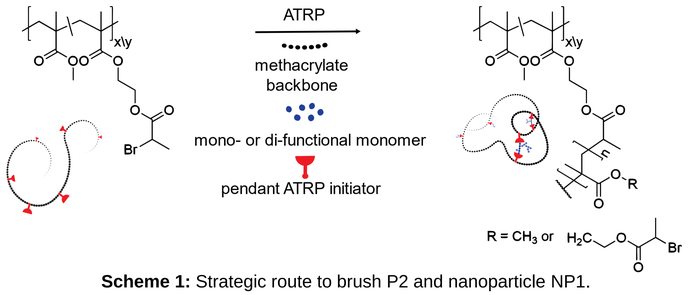
Introduction

With the goal of creating functionalized single-chain nanoparticles (SCNP) with tunable nanoenvironments, we investigated the intra-chain ATRP of pendant bromopriopionate-decorated poly(methyl methacrylates). Parent polymer P1 was synthesized using RAFT. The pendant bromopropionate groups were used to initiate intra-chain polymerization under conditions favoring termination by coupling. MMA and initiator-functionalized monomers, M1, were used to prepare brush (P2) and SCNP (NP1) examples.



Scheme 1: Strategic route to brush P2 and nanoparticle NP1.

Formation of SCNP by ATRC

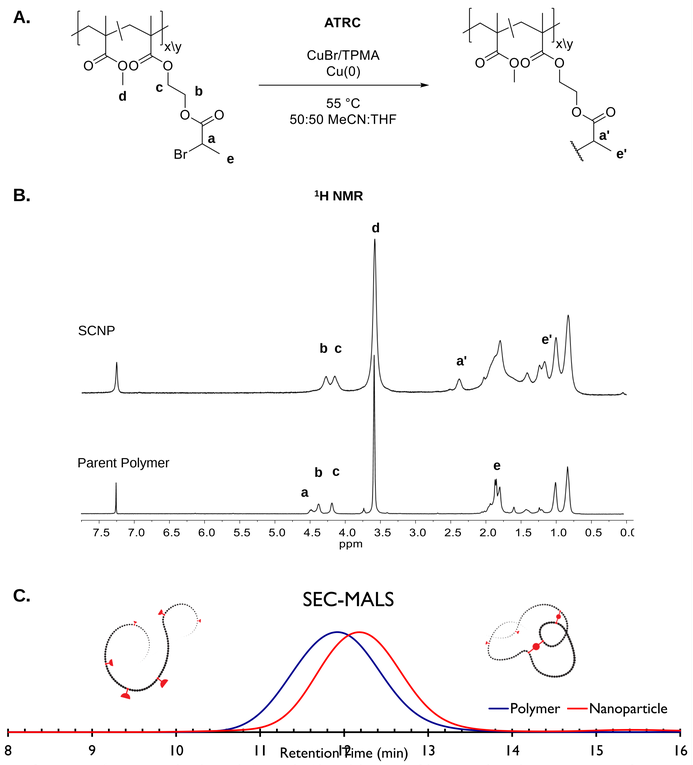


Figure 1: ^{1}H NMR (1B) and GPC (1C) evidence of intramolecular atom transfer radical coupling to form SCNP (1A).[1]

Tracking Intra-chain ATRP and Coupling

Because of the wide variety of monomers compatible with copper-mediated polymerizations, the design imparts handles with which to control both architecture and functionality in SCNP. Figure 2 shows SEC-MALS traces for the parent chain P1 and corresponding SCNP, NP1. The molecular weight as determined by MALS increased after polymerization, and the shift to a longer retention time is consistent with the successful formation of SCNP through ATRC between the pendant alkyl bromide units. As a control, the procedure was repeated using MMA as a monomer, removing the polymer's ability to participate in ATRC. The expected increase in molecular weight was this time accompanied by a shift to a shorter retention time, which is consistent with the formation of the anticipated brush polymer.

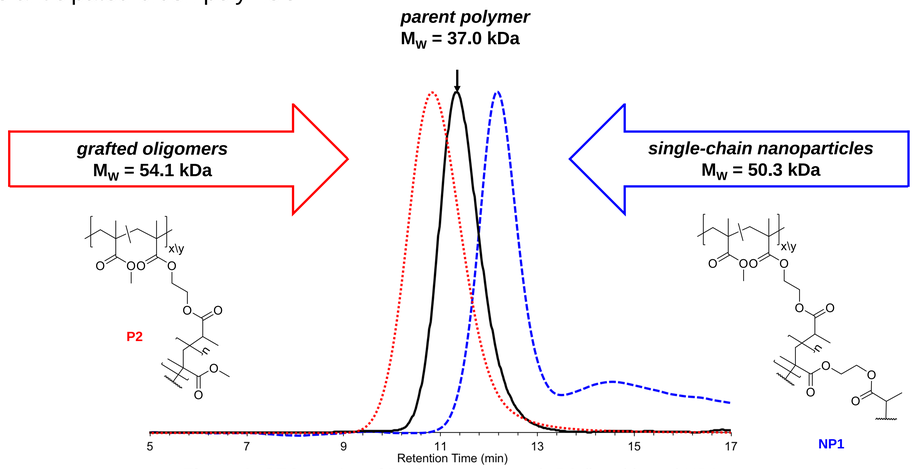


Figure 2: SEC overlay of P1 (parent polymer), P2 (brush), and NP1.

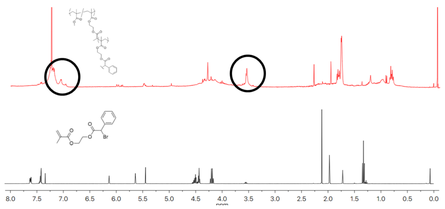


Figure 3: ^{1}H NMR overlay of PhBrema and corresponding SCNP.

	M_n (kDa)	Đ	$R_h(v)_n$ (nm)	$[\eta]_n$ (mL/g)	M-H-S alpha
Parent Chain	**13.6**	**1.11**	**3.8**	**25.3**	**0.65**
Hyperbranched SCNP	**36.7**	**1.40**	**3.7**	**47.6**	**0.77**

- *Retention time increases*
- *Absolute molecular weight from MALS detector increases*
- *Hydrodynamic radius comparable or smaller*

Average conversion of 50% in 24 h; 85% of bromide units remained unreacted.

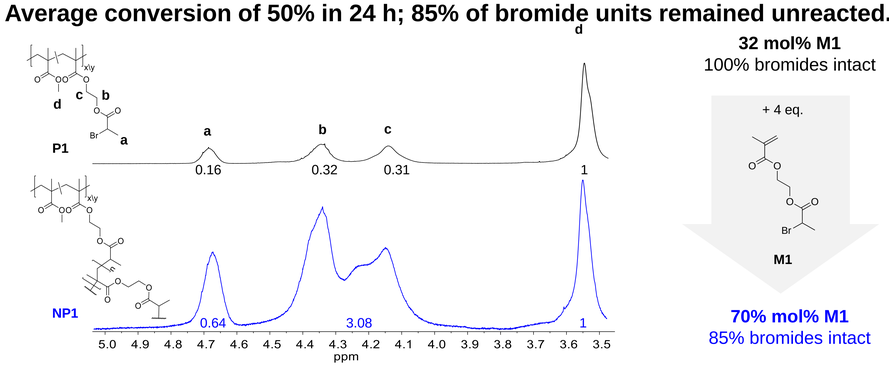


Figure 4: ^{1}H NMR overlay of P1 and NP1 showing the incorporation of additional functional monomer, highlighting the region featuring methacrylolyl and alkyl bromide signals of interest.

Limiting Disproportionation

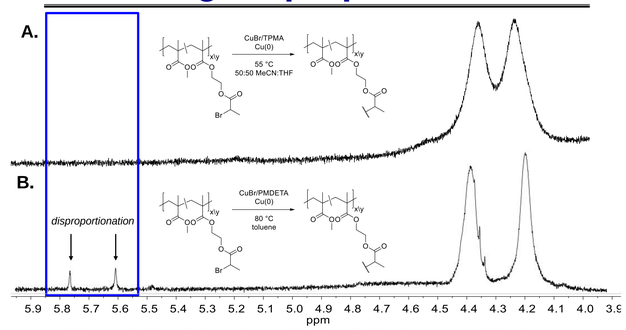


Figure 4: Careful catalyst selection limits the competition from disproportionation, favoring bimolecular termination.

Because our design relies on bimolecular coupling (ATRC) to form SCNP, it is important to limit competition from disproportionation. To do so, we relied on the rich body of ATRP literature to select appropriate catalysts and reaction conditions. Figure 4 compares the ^{1}H NMR spectrum of the product obtained using a PMDETA/CuBr solution in toluene (4B) with that obtained using TPMA/CuBr in acetonitrile and THF (4A). Vinyl resonances from disproportionation products appear exclusively in 4B. This result informed our choice of reaction conditions throughout this work.

Summary and Conclusions

We found that poly(methyl methacrylates) decorated with pendant bromopriopionate units can be converted to SCNP using a facile intra-chain polymerization process. Our early findings suggest that the coupling of a small proportion of the chains drives SCNP formation while the majority of pendant ends remain active. This speaks to the possibility of building more complex systems through further functionalization or chain extension. We are currently working to exploring this potential with the hope of creating a framework conductive to the modular addition of application-specific functionalities to a controlled SCNP environment.

Acknowledgements

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References

1. Hanlon, A.M.; Chen, R.; Rodriguez, K.J.; Willis, C.; Dickinson, J.G.; Cashman, M.; Berda, E.B., "Scalable Synthesis of Single-Chain Nanoparticles under Mild Conditions". *Macromolecules* **2017**.