Styrenic star polymers incorporating a range of comonomers via RAFT

Jacob A. Bryant, Kathleen Huynh, Melissa S. Griffin, Sadaf Omar, Rachel Chiang, Madalyn R. Radlauer
Department of Chemistry, San Jose State University, San Jose, CA 95192-0126, USA

Background

- Star polymers are structured polymers that consist of linear "arms" branching out from a crosslinked "core".
- The structure of these polymers makes them applicable to a range of uses including as viscosity modifiers, for drug encapsulation, or for site-isolation of chromophores or catalysts.
- Literature reports on the synthesis of styrenic star polymers by reversible addition fragmentation chain transfer (RAFT) polymerization showed low arm incorporation, low yield, and high dispersity.
- Solubility tests and Reagent Ratios were conducted by previous members of the Radlauer Research Group in the early stages of Star Polymer research.

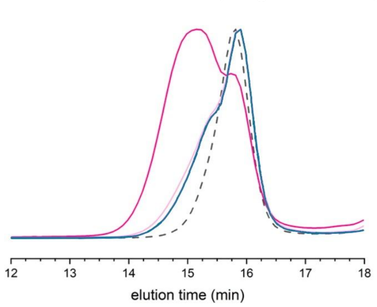


Figure 1. Poly Tert Butylstyrene star polymers in different solvents.

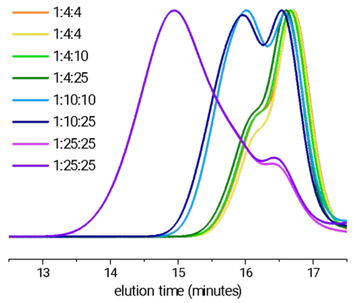
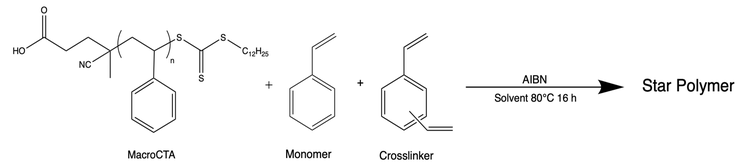


Figure 2. Polystyrene reproducibility runs of MacroCTA:Crosslinker:Monomer.

(1) Rodionov, V.; Gao, H.; Scroggins, S.; Unruh, D. A.; Avestro, A. J.; Fréchet, J. M. J. Easy Access to a Family of Polymer Catalysts from Modular Star Polymers. *J. Am. Chem. Soc.* 2010, *132* (8), 2570–2572.
(2) Ferreira, J.; Syrett, J.; Whittaker, M.; Haddleton, D.; Davis, T. P.; Boyer, C. Optimizing the Generation of Narrow Polydispersity "Arm-First" Star Polymers Made Using RAFT Polymerization. Polym. Chem. **2011**, 2 (8), 1671–1677.https://doi.org/10.1039/c1py00102g.

Why RAFT?



Scheme 1. General procedure to synthesize our star polymers.

RAFT polymerization employs a chain-transfer agent (CTA) and a radical initiator for controlled radical polymerization. The benefits to RAFT include the ability to use a wide array of monomers, as well as exert control over polymer size and dispersity.

Characterization via GPC

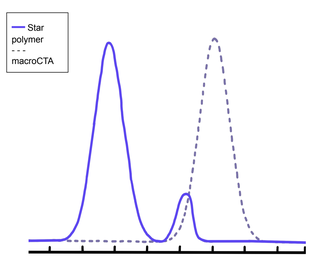


Figure 3. Star polymer chromatogram showing remaining homopolymer.

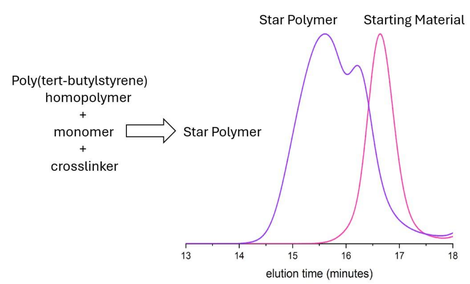


Figure 4. General understanding of a successful star polymer reaction using tert-butylstyrene comonomer.

- After synthesis, our star polymers are characterized with gel permeation chromatography (GPC).
- Verification of polymerization and consistency in the products are analyzed using this size-exclusion chromatography method.
- Star polymers with low dispersity (narrow peaks) and larger size are the target goal.

(3) Perrier, S. 50th Anniversary Perspective: RAFT Polymerization—a User Guide. *Macromolecules* **2017**, *50* (19), 7433–7447.
(4) Artar, M.; Terashima, T.; Sawamoto, M.; Meijer, E.W.; Palmans, A. R. A. *J. Polym. Sci. Part A Polym. Chem.* **2014**, *52* (1), 12–20.
(5) Biewend, M.; Neumann, S.; Michael, P.; Binder, W. H. *Polym. Chem.* **2019**, *10*, 1078–1088.

Collection of Tested Comonomers

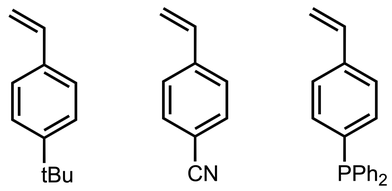


Figure 5. Range of Comonomers Tested as Star Polymers.

In order to better understand the potential of this star polymer synthesis method by RAFT, a range of monomers and comonomers were investigated.

GPC Data of Comonomer Runs

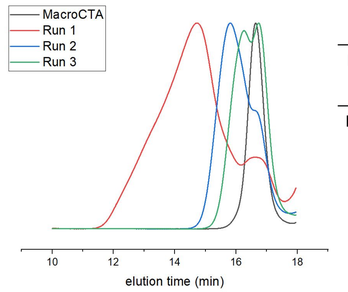


Figure 6. tBuS overlay of replication runs. Run 1 solubilized in MeCN. Run 2 subilized in cyclohexane. Run 3 solubilized in toluene. overlay reactions tbS 73, 74, 77

PS x tBuS Table

Reaction	Percent Yield	Number of Arms	Molecular Weight	Dispersity
MacroCTA	-	-	1680	-
Run 1	85%	343.9*	1719566	3.45
Run 2	75%	10.4	52114	1.03
Run 3	53%	5.3	26515	-

Table 1. Quantitative data for tBuS star polymers over three different reactions with varying solvents.

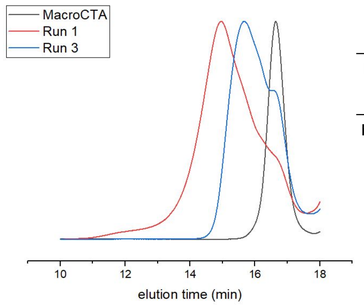


Figure 7. CN overlay of replication runs. Run 1 solubilized in MeCN. Run 2 was insoluble gel when solubilized with cyclohexane. Run 3 was solubilized in toluene. CNS 75, 76, 78

PS x CN Table

Reaction	Percent Yield	Number of Arms	Molecular Weight	Dispersity
MacroCTA	-	-	1680	-
Run 1 (MeCN)	81%	38.8	193940	1.59
Run 2 (Cyclo)	-	-	-	-
Run 3 (toluene)	74%	8.1	40421	1.01

Table 2. Quantitative data for CN star polymers over three different reactions with varying solvents.

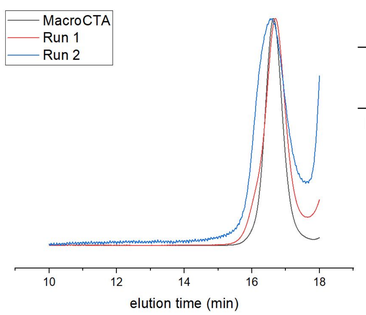


Figure 8. DPPST overlay or replication runs.Run 1 was solubilized in MeCN. Run 2 was solubilized in cyclohexane. 34, 38

PS x DPPST Table

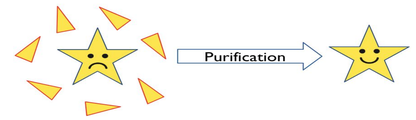
Reaction	Percent Yield	Number of Arms	Molecular Weight	Dispersity
MacroCTA	-	-	1680	-
Run 1 (MeCN)	64%	3.6	21778	-
Run 2 (Cyclo)	66%	138.4	830334	-

Table 3. Quantitative data for DPPST star polymers over two different reactions with varying solvents.

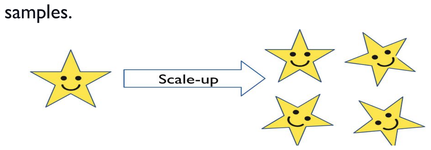
Discussion

- Across all star polymers synthesized the percent yield, number of arms, molecular weight and dispersity showed improved results in comparison to initial MacroCTA.
- Shifts upstream in GPC peaks indicates successful formation of star polymers.
- The results across comonomer runs demonstrates consistency with RAFTs tolerance of a wide range of functional groups.
- 'Arm-first' polymerization method via RAFT exhibited improved quantitative data from previous literature.
- DPPST shows signs of potential issues during synthesis which will be refined and improved.

Purification and Scale-Up



1. Purification of star polymers is important in developing pure stars for future reactions. BioRad beads contain semi-permeable membranes which utilize size-exclusion techniques that will allow for impurities within our future star polymers to be separated based on known molecular weights within our samples.



2. Increased quantities of reagents have caused difficulties in star polymer synthesis that result in a range of polymerization issues. Scaling up our 0.2 g reactions to multigram scale reactions will allow for higher yields of purified star polymers.

Applications in Catalysis

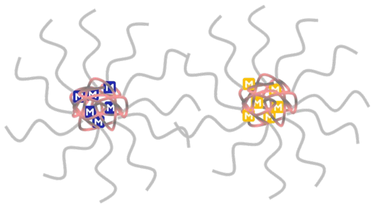


Figure 9. Depiction of metallated star polymers for enzyme-like catalysis.

- In the future we also plan to incorporate copper-, ruthenium-, iridium- and iron-containing catalyst complexes in our star polymer cores.
- Incorporation of these metal catalysts into our star polymers will work towards our goal of examining the effects of a polymer scaffold on supported catalysts.

Acknowledgements

Research Initiative for Scientific Enhancement (RISE) Program (R25)
NIH NIGMS AREA R15
1R15GM132857-01A1

SJSU SAN JOSÉ STATE UNIVERSITY
College of Science
Department of Chemistry

Subgroups Members:
Star Polymer: Kathleen Huynh, Sadaf Omar, Rachel Chiang, Melanie Gonzalez, Melissa Griffin

CSU LSAMP
NSF-MRI
CHE
1917786

