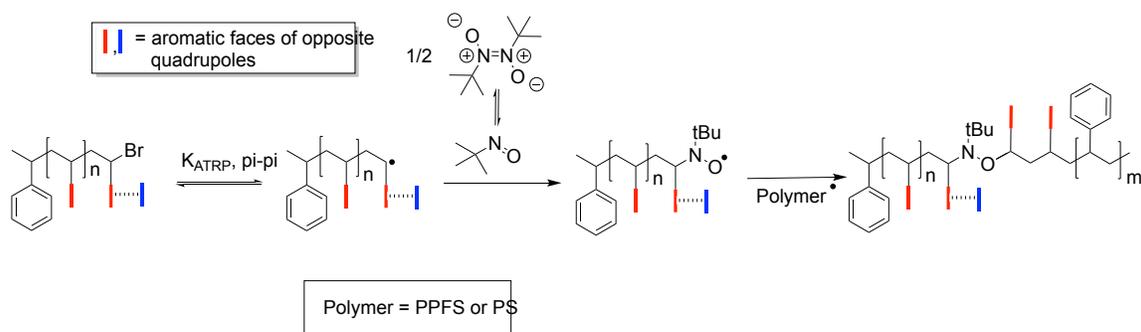


PRF# 56381-UR7

b. Project Title: Stereoregular Vinyl Polymers Prepared By Pi-pi Stacking Interactions

c. Principal Investigator Name, Affiliation: Eric Tillman, Santa Clara University

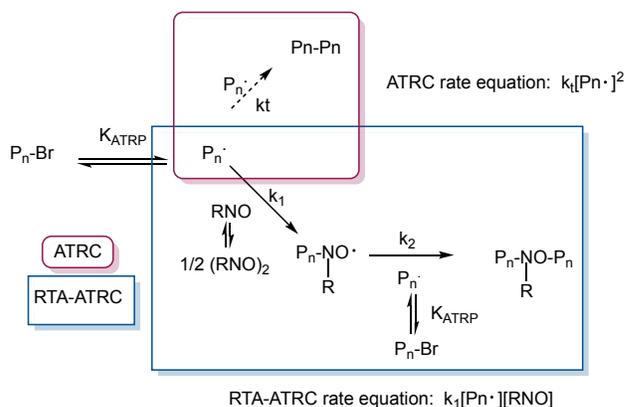
d. Co-PI name (if any), Affiliation



Scheme 1. Pi-pi stacking in radical trap-assisted atom transfer radical coupling of polystyrenes. We have focused on how this affects the rate that the final coupled product is formed.

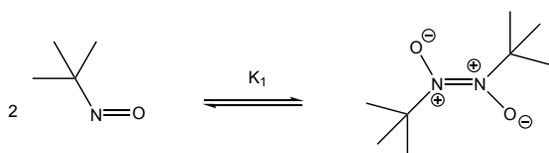
Main finding: The addition of aromatic faces to atom transfer radical coupling (ATRC) reactions has been found to alter the extent of coupling by affecting both K_{ATRP} and the reactivity of the radical trap. Electron rich faces, such as benzene, increased the reactivity of the radical trap 2-methyl-2-nitrosobenzene (MNP), while the electron poor hexafluorobenzene shifts the K_{ATRP} further towards the active radical.

Summary: Monobrominated poly(pentafluorostyrene) (PPFSBr), polystyrene (PSBr), and poly(methyl acrylate) (PMABr) were prepared by atom transfer radical polymerization (ATRP) and then used in a variety of atom transfer radical coupling (ATRC)-type reactions to observe the impact of external aromatic faces on the extent of coupling (X_c). These coupling reactions are summarized in Scheme 2. In ATRC reactions assisted with the radical MNP, X_c was nearly unchanged when the electron rich benzene co-solvent (50% v/v with THF) was replaced with the electron poor hexafluorobenzene (HFB) for PSBr and PMABr. In the case of PPFSBr, the addition of benzene to the reaction mixture resulted in far lower extents of coupling ($X_c < 0.2$). ^1H NMR spectra of the radical trap MNP in HFB showed greater aggregation to the inactive form, compared to spectra obtained in benzene. To remove the effect of the radical trap interacting with the aromatic co-solvent and altering the rate of coupling, traditional ATRC reactions were performed with the same co-solvent systems and, in this case, HFB resulted in higher X_c values across all polymer types. This is consistent with HFB pushing the position of the K_{ATRP} further towards the active radical, while benzene increased the reactivity of the MNP radical trap.



Scheme 2. Mechanistic and kinetic comparison of atom transfer radical coupling (ATRC) and radical trap-assisted ATRC (RTA-ATRC).

We have recently submitted a paper to *Macromolecular Chemistry and Physics* that the results outlined above. The initial motivation of this work was to gauge how pi-pi stacking would impact coupling reactions by adjusting the stability of the polymer radical and, therefore, K_{ATRP} . Our results, however, indicate that pi-pi stacking is not the major driving force in altering the rate of the coupling reaction, and the addition of the electron deficient HFB, compared to benzene, increases the magnitude of K_{ATRP} , while simultaneously promoting aggregation of the MNP radical trap (Scheme 3). The overall effect is an increase in the rate of ATRC reactions performed in the presence of HFB across all polymer types, compared to benzene, yet a cancellation of this improvement in analogous RTA-ATRC reactions. The GPC traces of PPFsBr undergoing dimerization can be visualized in Figure 1.



Scheme 3. Aggregation of nitroso dimer (MNP) to the active monomeric form, capable of trapping polymer radicals. Only the monomeric form is expected to participate in RTA-ATRC reactions.

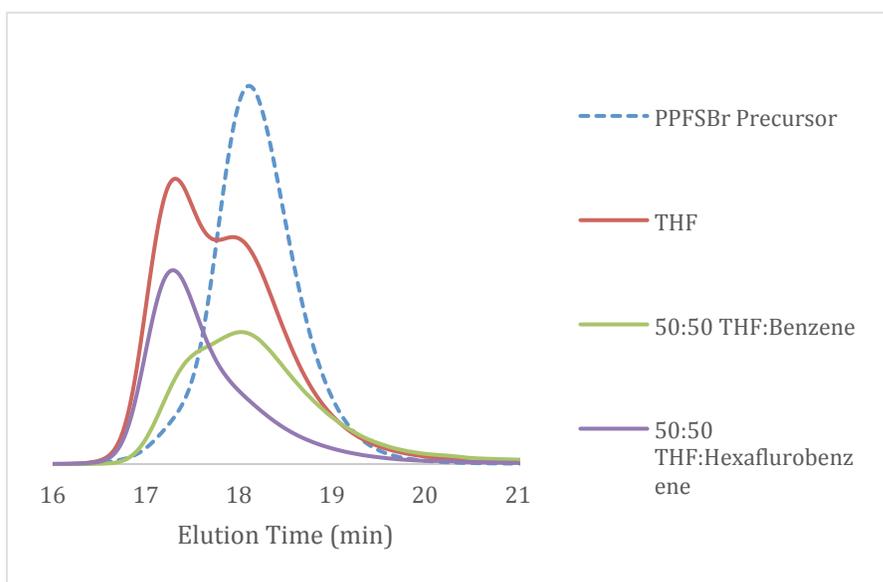


Figure 1. GPC traces of PPFsBr precursor prepared by ATRP and the RTA-ATRC products after 60 min using MNP as the radical trap in various solvents. $[PPFsBr] = 10 \text{ mM}$; $[PPFsBr]:[MNP_{monomer}]:[Cu^0]:[CuBr]:[PMDETA] = 1:0.6:1:1:2$; Temperature = 22°C .