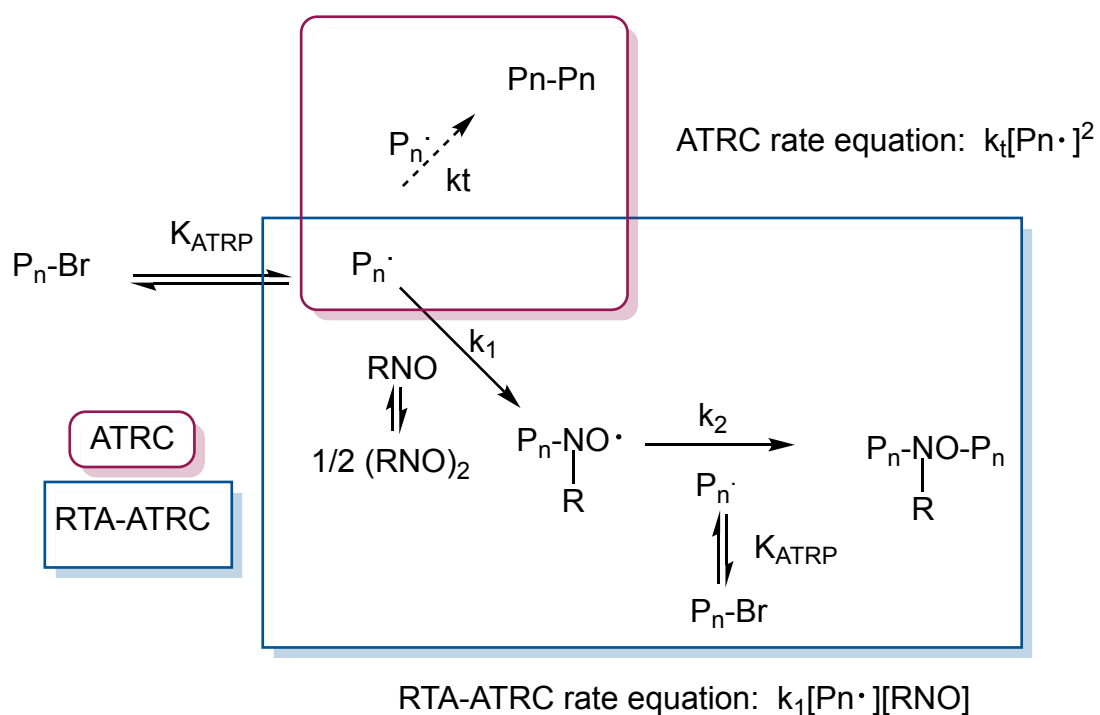


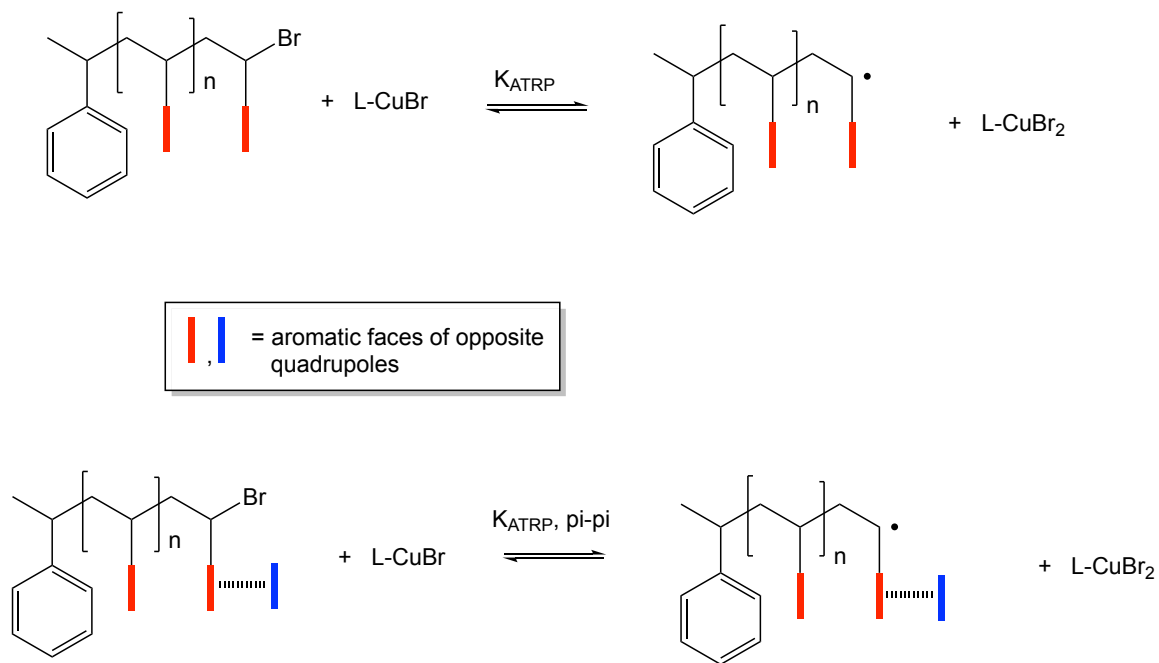
Atom transfer radical coupling (ATRC), with or without radical traps (radical trap-assisted ATRC; RTA-ATRC), is an effective chain end-joining reaction that can be used to create new topologies and block copolymers. These chain end coupling variations are compared mechanistically and kinetically in Scheme 1. Note that the magnitude of  $K_{\text{ATRP}}$  plays a role in the rate of coupling in both cases, but plays a greater role in ATRC reactions lacking a radical trap. Furthermore, the ability of 2-methyl-2-nitrosobenzene (MNP) to trap a polymer radical, ( $k_1$  in Scheme 1), is tied to the polarity of the solvent, which alters the aggregation and reactivity of the radical trap towards the alkyl radicals.



**Scheme 1.** Mechanistic and kinetic comparison of atom transfer radical coupling (ATRC) and radical trap-assisted ATRC (RTA-ATRC).

Pi-pi stacking between electron rich/poor external aromatic faces and vinyl aromatic polymer could impact the ability of the polymer to stabilize a chain end

radical, altering  $K_{\text{ATRP}}$  and ultimately the efficiency of ATRC or RTA-ATRC reactions. Additionally, aromatic co-solvents may result in  $\text{Cu(II)Br}_2$  stability changes (Scheme 2), as the halophilicity of the  $\text{Cu(II)}$  is known to be solvent dependent.



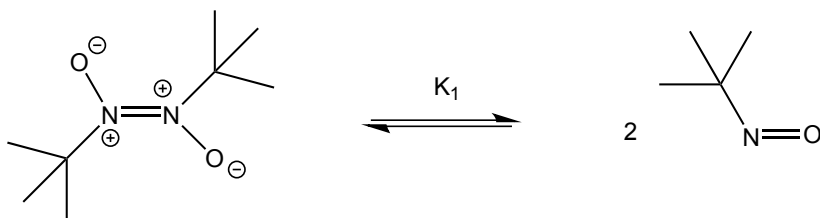
**Scheme 2.** ATRP equilibrium in the presence and absence of potential pi-pi stacking additives. Note that the stability of the catalyst-ligand complexes (where L = ligand) may also be affected by the solvent composition, which would also alter the  $K_{\text{ATRP}}$ .

We are currently studying and preparing to publish the effect of aromatic co-solvents, as potential pi-pi stacking additives, on the extents of dimerization of PSBr, fluorinated PSBr, and non-aromatic vinyl polymers (PMABr) in ATRC and RTA-ATRC reactions. 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,  $K_{\text{ATRP}}$ . Our results, however, indicate that pi-pi stacking is not the major driving force in altering the rate of the coupling reaction, and the

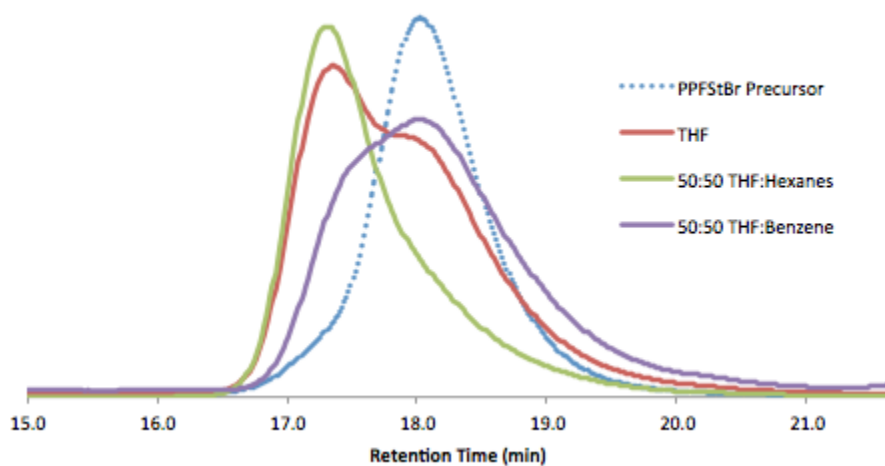
addition of the electron deficient HFB, compared to benzene, increases the magnitude of  $K_{\text{ATRP}}$ , while simultaneously promoting aggregation of the MNP radical trap. The overall effect is an increase in the rate of ATRC reactions performed in the presence of HFB across all polymer types, compared to benzene, yet a cancellation of this improvement in analogous RTA-ATRC reactions.

Brominated poly(pentafluorostyrene) (PPFS), prepared by ATRP, was used in a series of RTA-ATRC reactions in order to gauge the impact of an external aromatic face on the extent of coupling ( $X_c$ ) after 1 h. Surprisingly, PPFS was found to undergo substantial dimerization at room temperature in THF or equi-volume THF/hexanes as the reaction medium and MNP as the radical trap. The superior coupling of the mixed solvent system of THF and hexanes has been previously demonstrated with PSBr, which can be rationalized by the equilibrium of the MNP radical trap: the addition of nonpolar co-solvents shifts the position further towards the active monomeric form of the radical trap (Scheme 3). When benzene was added as the co-solvent and pi-pi stacking participant, the extent of dimerization after 1 h was reduced, compared to the hexanes as the co-solvent, and found to be less than 50% ( $X_c = 0.45$ ). When the identical RTA-ATRC reaction was performed using HFB as the co-solvent, creating a scenario where both the polymer pendant groups and additive possessed electron deficient aromatic faces, the extent of coupling was similar to when performed in the presence of benzene ( $X_c = 0.40$  compared to 0.45). The GPC traces of the

PPFSBr precursor and RTA-ATRC products using MNP as the radical trap are shown in Figure 1.



**Scheme 3.** Dissociation 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 PPFStBr precursor prepared by ATRP and the RTA-ATRC products after 60 min using MNP as the radical trap in various solvents. [PPFSBr] = 10 mM; [PPFSBr]:[MNP<sub>monomer</sub>]:[Cu<sup>0</sup>]:[CuBr]:[PMDETA] = 1:0.6:1:1:2; Temperature = 22°C.