# Cationic RAFT Polymerization of Styrenic Monomers

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Reversible addition-fragmentation chain-transfer (RAFT) radical polymerization is a one of the most versatile and powerful polymerization techniques not only for the synthesis of (co)polymers with certain composition, controlled molecular weights and target functionality but also advanced macromolecular architectures (block-, graft-, star-shape, etc.) for diverse fields of applications.[1] Recently, the cationic RAFT polymerization was discovered that opens new possibilities to synthesize unique block copolymers via mechanistic transformation from radical to cationic polymerization.[2] Particularly, dithiocarbamates and xanthates as chain-transfer agents (CTA*s*) showed high efficiency in cationic RAFT polymerization of vinyl ethers affording well-defined polymers with low dispersity up to $M_n$=100,000 g mol$^{-1}$.[2] However, the efficiency of the above-mentioned CTAs in the cationic RAFT polymerization of p-methoxystyrene (pMOS) is much lower and zero efficiency was observed in polymerization of less reactive monomers.

In this work, the successful cationic RAFT polymerization of p-methoxystyrene (pMOS) with different dithiobenzoates as chain-transfer agents activated by very small amount of Lewis acid will be discussed. We will demonstrate that through rational design of the CTA structure the well-controlled cationic RAFT polymerization of pMOS could be achieved at room temperature to afford poly(p-methoxystyrene) with $M_n$ up to 35,000 g mol$^{-1}$ and low dispersity ($Đ \leq 1.25$). The further design of CTA*s* for performing cationic RAFT polymerization of less reactive monomers such as p-methylstyrene and styrene consisted in the introduction of electron-withdrawing groups into CTA structure. Cationic RAFT polymerization of less reactive p-methylstyrene and styrene was performed using CTAs bearing electron-withdrawing groups to give polymers with controlled molecular weight up to $M_n$< 10,000 g mol$^{-1}$ (poly(p-methylstyrene)) and $M_n$< 5,000 g mol$^{-1}$ (polystyrene) and moderate dispersity ($Đ$=1.8–2.2). The developed initiating systems showed high efficiency toward cationic RAFT (co)polymerization of bio-based monomer anethole.

**Keywords:** cationic polymerization, RAFT polymerization, controlled polymerization

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## References

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