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OUTER-SPHERE-ELECTRON-TRANSFER METAL-CATALYZED POLYMERIZATION OF STYRENE USING A MACROBICYCLIC LIGAND

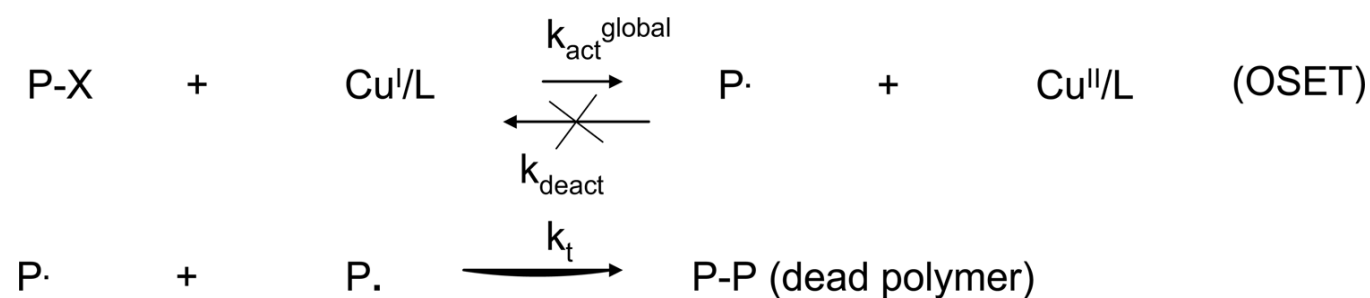
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Atom Transfer Radical Polymerization (ATRP) is a successful method for the preparation of macromolecules with narrow polydispersity. The pioneering work conducted by Matyjaszewski *et al*¹ and Percec *et al*² and research conducted thereafter has shown that this technique is very versatile, enabling a large number of monomer species to be polymerized. The technique can be used over a wide range of experimental conditions, i.e. in organic or protic media, and in water based heterogeneous emulsion polymerisations.

In this work³, CuBr-catalyzed polymerizations of styrene in the presence of a macrobicyclic mixed donor (N and S) encapsulating ligand, NH₂captan, were carried out in toluene at 60 and 100 °C. The external orders of reaction in [CuBr], [NH₂captan], and [CuBr₂] were found to be 0.5, 0.5, and close to zero, respectively, in agreement with the postulated mechanism (Scheme 1) of little or no deactivation of polymeric radicals and a significant amount of bimolecular termination. This proved an ideal method for radical coupling experiments to make high-molecular weight multiblock copolymers from difunctional PSTY (Br-PSTY-Br, PDI = 1.11).



Scheme 1. Mechanism for capture of Cu^{II} by the cage ligand, NH₂captan, of styrene polymerization in the presence of CuBr.

- (1) Wang, J.-S.; Matyjaszewski, K. *Macromolecules* **1995**, *28*, 7901-7910.
- (2) Percec, V.; Barboiu, B. *Macromolecules* **1995**, *28*, 7970-7972.
- (3) Bell, C. A.; Whittaker, M. R.; Gahan, L. R.; Monteiro, M. J. *J. Polym. Sci. Part A: Polym. Chem.* **2007**, *46*, 146-154.