

# Bromine transfer to a Cu complex to activate an ARGET ATRP reaction

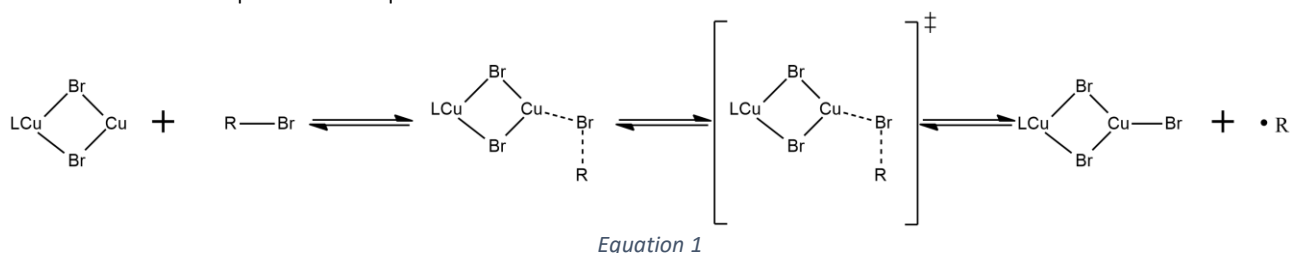
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Atom Transfer Radical Polymerization (ATRP) is a versatile polymerization technique. However, the catalytic mechanism is yet to be determined. To investigate this mechanism we considered the reaction model reported in Equation 1



where L = BPY, BPY<sub>2</sub>, Me<sub>6</sub>TREN and R=CH<sub>3</sub>Br, ethyl bromoacetate (EBAc), ethyl  $\alpha$ -bromoisobutyrate (EBIB). While we know that the global reaction is endothermic, we still do not have the transition barriers for all the cases involved. In fact it can be easily noted there is a change in the spin state between reactant (singlets) and products (doublet), thus an uncertainty on the spin state of the transition state we encounter (singlet or triplet). Our first lead in this investigation has been the work from Fang et al. [1], where the authors proposed an inner sphere electron transfer transition state for a similar, albeit smaller system. Therefore we employed the 6-31++G(d,p) basis set at B3LYP level of theory to optimize products, reactants and singlet and triplet intermediates. From there we performed PES scans along the C-Br bond, searching for a transition state. Eventually, through a subsequent broken symmetry approach, we were able to locate some of them in an open shell singlet state. However the structures we found (Figure 1) are deeply different from the ones previously known, in fact our geometries suggest a dissociative mechanism to form the radical, due to the distance measured between carbon and bromine (greater than 3.5  ). This variation can aid to investigate on the ATRP mechanism from an other point view, possibly enhancing our comprehension of the mechanism of this reaction. Indeed our plan is now to start from the kinetic constants we are obtaining for the open shell singlet to simulate the evolution of the reaction through Kinetic Monte Carlo method.

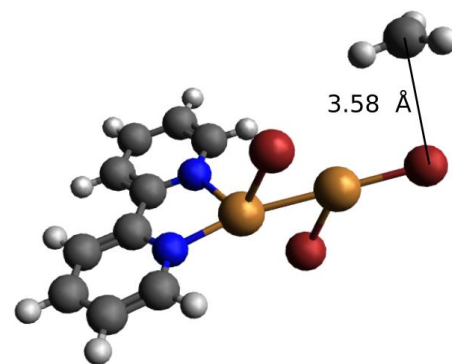


Figure 1: BPYCuBr<sub>2</sub>CuBrCH<sub>3</sub> singlet open shell TS calculated at B3LYP level of theory with 6-31++G(d,p) basis set.

[1] *J. Am. Chem. Soc.* 2019, 141, 18, 7486–7497 Fang, C. Fantin, M. Pan, X. de Fiebre, K. Coote, M. L. Matyjaszewski, K. Liu, P.