

Computational Study of Chain Transfer Reactions in High-Temperature Polymerization of Alkyl Acrylates

Nazanin Moghadam

Advisor: Prof. Masoud Soroush

Co/advisor: Prof. Andrew Rappe

Abstract

The research presents a computational study of chain transfer to monomer (CTM) and chain transfer to polymer (CTP) reactions in self-initiated high-temperature homo-polymerization of alkyl acrylates (methyl, ethyl and *n*-butyl acrylate). We studied possible mechanisms of CTM and CTP. The effects of the length of live polymer chains and the type of monomer-self-initiated mono-radical (M_1^\bullet vs. M_2^\bullet) that initiated the live polymer chains, on the energy barriers and rate constants of the mechanisms were investigated theoretically. All calculations were carried out using density functional theory. Four types of hybrid functionals (B3LYP, X3LYP, M06-2X, and WB97X-D) and four basis sets (6-31G(d), 6-31G(d,p), 6-311G(d), and 6-311G(d,p)) were applied to predict energy barriers and the molecular geometries of the reactants, products, and transition states. Transition state theory was used to estimate rate constants. It was found that abstraction of a hydrogen atom (by live polymer chains) from the methyl group in methyl acrylate, the methylene group in ethyl acrylate, and methylene groups in *n*-butyl acrylate are the most likely mechanisms of CTM. The most favorable mechanism for CTP was abstraction of hydrogen by live polymer chains from dead polymer tertiary carbon atom. No significant change in the rate constant values was observed as the length of live polymer chains was increased. Live chains initiated by M_2^\bullet or M_1^\bullet were found to be capable of participating in CTM and CTP. Abstraction of a hydrogen by a tertiary radical in CTM reaction has a higher energy barrier than that by a secondary radical, which agrees with experimental findings. Based upon these, we suggest that CTM occurs via hydrogen abstraction by live polymer chains from the methyl group of methyl acrylate and methylene group(s) of ethyl (*n*-butyl) acrylate and CTP occurs via hydrogen abstraction from tertiary carbon atom of the dead polymer.