Reactivity of thiocarbonyls compounds in RAFT Polymerization: An ab initio Study

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Abstract

In recent years, the field of free-radical polymerization has been revolutionalized by the development of controlled/living radical polymerization processes, including nitroxide-mediated polymerization (NMP)[1], atom transfer polymerization (ATRP)[2], and reversible addition fragmentation chain transfer (RAFT) polymerization[3].

In the present study we analyze the reaction mechanisms involved by Xanthates (S-(C=S)-O) and thiocarbonates (O-(C=S)-O) compounds in reversible addition fragmentation chain transfer (RAFT) polymerization. For the purpose, theoretical calculations have been performed by means of density functional theory (DFT), using B3LYP, CAM-B3LYP, LC-wPBE exchange correlation functional and 6-31G* basis sets. Thanks to the variational transition state theory, the rates of addition and fragmentation reaction were obtained.

Keywords: DFT calculation, thiocarbonyls compounds, RAFT agents.

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