

Thermodynamics and Kinetics of in situ Nitroxide Mediated Polymerization

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Controlled radical polymerization (CRP) is a promising polymerization technique that enables to produce well-defined, end-functionalized polymers at milder experimental reaction conditions than living ionic polymerization. An interesting and polyvalent CRP method is Nitroxide Mediated Polymerization (NMP). The control of the NMP process is based on a reversible recombination between propagating species ($P\bullet$) and nitroxide ($R_2NO\bullet$, R = alkyl group) with the formation of alkoxyamine (R_2NOP , R = alkyl group), resulting in a low radical concentration and, hence, leading to a suppression of undesired termination reactions. A recently developed type of NMP is in situ nitroxide mediated polymerization (in situ NMP), where the nitroxide and alkoxyamine are formed in the polymerization medium itself, based on precursors such as nitrones ($RN(O)=CHR$, R = alkyl group), nitroso compounds ($RN=O$, R = alkyl group) etc. In this work, a quantum chemical study is presented reporting thermodynamic and kinetic data obtained at various levels of theory for a set of compounds and reactions related to in situ NMP. The selection of a cost-efficient method to study these was done by comparison of calculated ab initio data with experimental data or with values obtained from high level G3B3 calculations. Subsequently, the most appropriate level of theory was applied to the calculation of nitroxide- and alkoxyamine-forming reactions of a typical initiating system comprising 2,2'-azobisisobutyronitrile (AIBN), styrene and a nitron. Following relevant nitrones were considered: N-tert-butyl-alpha-isopropyl nitron, N-tert-butyl-alpha-tert-butyl nitron, C-phenyl-alpha-tert-butyl nitron, N,alpha-diphenyl nitron, 5,5-dimethyl-1-pyrrolidin-N-oxide. The test set of the level of theory study consists of initiator-related compounds such as AIBN and benzoyl peroxide (BPO) and their radicals, monomer- and polymer-related structures, such as styrene, benzene, ethyl benzene and corresponding radicals, and also nitrones, nitroxides and alkoxyamines. Possible recombination/dissociation and addition/beta-scission reactions have been studied. For the level of theory study, several density functional theory (DFT) methods, such as B3LYP, B3P86, MPW1PW91, BB1K, BMK, BHandHLYP and the newly developed B2-PLYP and dispersion-corrected B97-D, were applied to the test set. In addition, various basis sets were examined, such as triple-zeta and quadruple-zeta, some containing polarization and diffuse functions. Composite methods, such as G3B3 and CBS-QB3, were also investigated, but merely as benchmarks. It was found that standard enthalpies of formation are best predicted by the composite methods (Mean Average Deviation from experiment ($MAD[exp]$) < 6 kJ mol⁻¹ for G3B3). These methods, however, are only applicable for the smallest molecules, hence, they were used only as benchmarks when no experimental data are available. Considering only the DFT methods, the B2-PLYP method is clearly the best performing with a $MAD[exp]$ < 10 kJ mol⁻¹ and $MAD[G3B3]$ < 14 kJ mol⁻¹. For larger systems, however, the MP2 contribution to the B2-PLYP results scales with N^5 (N being the number of basis functions), whereas regular DFT methods scale with N^3 . The order of increasing performance for the regular DFT methods is MPW1PW91, BMK, B97-D. For reaction enthalpies, BMK was found to outperform all other DFT methods with a $MAD[exp]$ < 5 kJ mol⁻¹, except for nitroxide-related structures for which a $MAD[exp]$ of 16 kJ mol⁻¹ was obtained. Moreover, BMK was shown to give an ideal trade-off between thermodynamics and kinetics and has been selected for the determination of quantum chemical parameters of the elementary reactions involved in (in situ NMP). Applying BMK to investigate the influence of the nitron structure on these elementary reactions shows significant differences between the various nitrones, as confirmed experimentally. Furthermore, this study offers a basis on which other nitron compounds may be evaluated for their use in (in situ NMP).