

Combining Metadynamics and Mean Force Integration for studying chemical reactions in solution: an application to backbiting of poly-Butyl Acrylate.

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Highlights

- Mean Force Integration and metadynamics allow discovering reaction pathways.
- Polar and non-polar solvents reduce the free energy barrier of activation by ~4 kcal/mol.
- Explicit treatment of solvent improves the agreement with experiments.

1. Introduction

Free radical polymerization (FRP) and pyrolysis processes are fundamental technologies with wide-ranging applications in fields such as material synthesis and recycling. Understanding the underlying reaction mechanisms and considering the effect of solvents is crucial for the design and scale-up of such processes. However, since pyrolysis lacks selectivity and radical intermediates are hard to measure due to their extremely short lifetimes, rate coefficients from experimental campaigns on this subject are scarce. Nevertheless, experiments on free radical polymerization have been a flourishing field of study in past two decades. Knowledge of rate parameters of elementary reactions in solution or in bulk is key for formulating a valid kinetic mechanism. To this day, individual kinetic rate parameters of radical chain propagations, depropagations as well as isomerizations (backbiting) can be accessed experimentally through Pulsed Laser Polymerization technique (PLP) coupled with Size Exclusion Chromatography (SEC) [1] as well as semibatch solution polymerization coupled with Nuclear Magnetic Resonance (NMR) [2]. The resulting rate coefficients are gathered in the IUPAC Database for standard monomers which represents the gold standard for the validation of theoretical calculations. In particular, the experimental studies taken as reference [1-2] report the propagation, backbiting and β -scission rate coefficients for poly-Butyl Acrylate in bulk and in solvent (mainly a mixture of ortho/meta/para-xylene). In this work, accelerated molecular dynamics in conjunction with Mean Force Integration (MFI) have been employed for exploring the free energy landscape of the backbiting of poly-Butyl Acrylate (PBA) in gas phase as well as in solution with non-polar (o-/m-/p-xylene) and polar (water) solvents. Then, rate constants are evaluated from the free energy barrier of activation based on the rare events generalized Transition State Theory (TST) [3].

2. Methods

The potential energy of the system has been partitioned such that the reactant molecule (i.e. the BA trimer) is described by a quantum tight binding potential (GFN1 xTB) whereas the surrounding solvent is treated with the classical Generalized Amber Force Field (GAFF). The electrostatic coupling between the reactant (QM) and the solvent environment (MM) has been modelled through a Coulomb potential. The free energy landscape is recovered from a metadynamics [4] simulation by means of the Mean Force Integration (MFI) algorithm implemented in [5]. This implementation of the MFI reconstructs an analytical expression for the mean thermodynamic force in the collective variables space $\nabla F_t(\mathbf{s})$ up to a given time t , where $F_t(\mathbf{s})$ refers to the Helmholtz free energy. As reported in [5,6], the mean force has two components, namely the gradient with respect to s of the natural logarithm of the biased probability density $p_b^t(\mathbf{s})$ and the gradient of the bias potential $V_t(\mathbf{s})$ accumulated up to time t , as shown in eq. (1).

$$\nabla F_t(\mathbf{s}) = -k_B T \nabla \ln p_b^t(\mathbf{s}) - \nabla V_t(\mathbf{s}) \quad (1)$$

Where k_B is the Boltzmann constant. The space of collective variables for the sampling of 1:5 backbiting is defined by the distance between the end chain radical and the hydrogen in fifth position (see Fig 1a).

3. Results and discussion

The results show that, on average, the interactions between reactant and solvent cause a ~ 4 kcal/mol reduction in the free energy barrier of activation toward the H-transfer, which allows to reach a better agreement with experimental data with respect to previous state-of-the-art calculations [7].

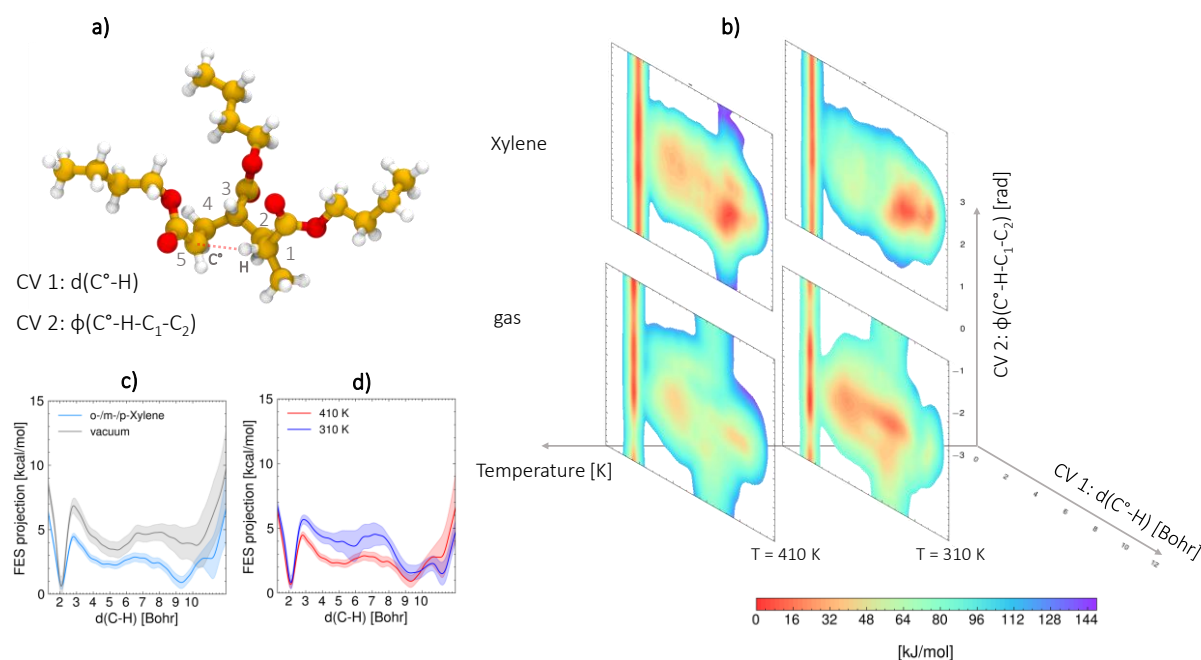


Figure 1. a) definition of the collective variables space $s(\mathbf{d}, \phi)$; b) Helmholtz free energy projected on the space of collective variables $s(\mathbf{d}, \phi)$ in gas phase and the presence of xylene solvent at 310 K and 410 K; c) projection of the free energy surface on the distance $d(\text{C-H})$ at 410 K with and without xylene solvent; d) parametric analysis on temperature of the free energy projection on the distance $d(\text{C-H})$.

4. Conclusions

In conclusion, the explicit treatment of the solvent in the study of intramolecular H-transfer reactions in solution allows to reduce the gap between theory and experiments in the estimation of intrinsic rate parameters.

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Keywords

Free Radical Polymerization; Metadynamics; Transition State Theory; Thermodynamic Integration.