

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

F. Serse*, A. Bjola**, M. Salvalaglio**, M. Pelucchi*

Francesco.serse@polimi.it

* CRECK Modelling Lab, Politecnico di Milano, Piazza Leonardo da Vinci 32, Milan, Italy;

** Thomas Young Centre and Department of Chemical Engineering, University College London, London, WC1E 7JE, United Kingdom

Abstract

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 (Fig. 1).

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 [3] simulation by means of the Mean Force Integration (MFI) algorithm implemented in [4]. 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 [4,5], 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).

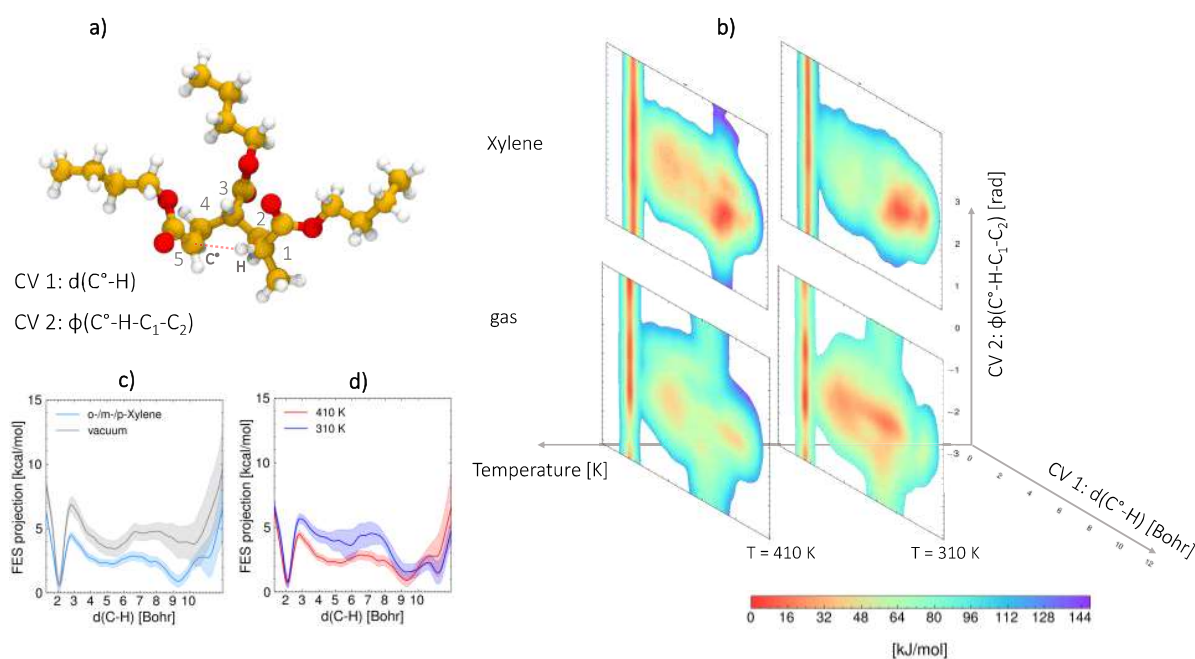


Figure 1. a) model molecule and CVs definition for the 1:5 backbiting; b) bivariate free energy surface in vacuum and in xylene solvent at 310 K and 410 K; c) marginal free energy profiles together with the standard deviation along the C-C distance in vacuum and in xylene solvent at T=410 K; d) marginal free energy profiles together with the standard deviation along the C-C distance in xylene solvent at 310 K and 410 K.

Rate constants are evaluated from the zero-point energy corrected free energy barriers of activation based on the rare events generalized Transition State Theory (TST) [6].

The newly found rate constants are introduced into a detailed kinetic mechanism from the literature [7]. In this previous study, the rate parameters of β -scission,

backbiting and tertiary propagation were used as degrees of freedom to match experimental profiles of monomer concentration. The introduction the kinetic parameters in xylene of backbiting as well as β -scission from our previous study [8] allow to match experiments using the tertiary propagation rate constant only as degree of freedom. The update kinetic scheme is reported in Table 1, whereas the predicted concentration profiles are shown in Fig. 2.

Table 1. Initiated radical polymerization mechanism of PBA.

Reaction	Pre-exponent (1/s)	Activation energy (J/mol)
Initiator decomposition	6.78E+15	147200
Propagation	1.80E+7	17400
Chain transfer to monomer	1.60E-2	15200
Tertiary propagation	7.90E+6	27800
Backbiting	1.88E+8	32600
β -scission	1.50E+13	88200
Termination	2.57E+8	2400
Chain transfer to solvent	176.00	32200

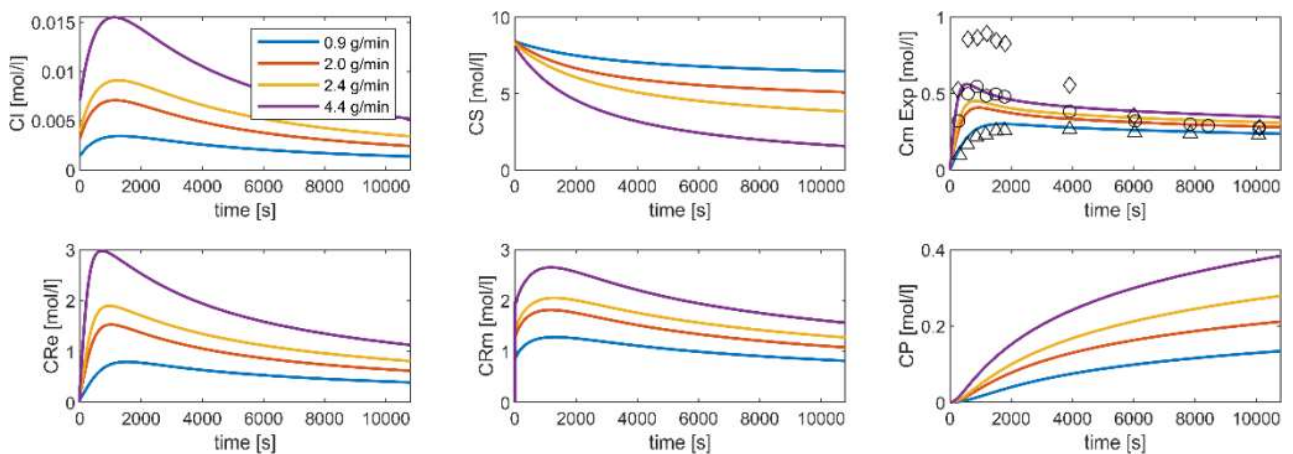


Figure 2. Concentration profiles in the starved feed semi-batch polymerization of PBA at 130°C for different monomer inlet flowrates. CI and CI. stand for initiator and its radical concentrations, CS stands for solvent concentration, Cm is the monomer concentration, CRe and CRm is the concentration of end-chain and mid-chain radicals, CP is the polymer concentration.

The updated mechanism is also applied to the thermal self-initiated polymerization of BA. A recent experimental study [] reported the effect of different solvents on the BA polymerization rates in a batch reactor allowing to validate our computational prediction of solvent effects on kinetic constants. In the absence of initiator I, the polymerization is triggered by thermal self-initiation. The Arrhenius parameters of this elementary reaction are unknown in the literature and have here been used as

degree of freedom to match the experiments. The values of this reaction that show better agreement with experiments in bulk is the following:

Reaction	Pre-exponent (1/s)	Activation energy (J/mol)	Order
Thermal self-initiation	7340	81600	0.3

Supposing that the solvent does not significantly affect thermal self-initiation, we show that solvent effects on the secondary reactivity, namely β -scission and backbiting, of BA can be responsible for the change in polymerization rate (Fig. 3).

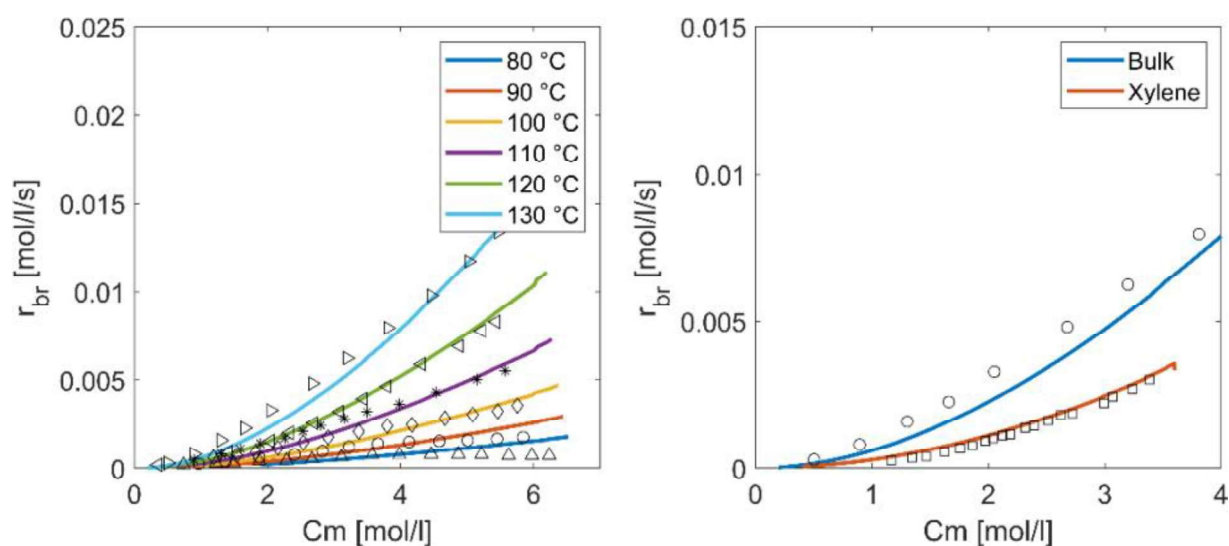


Figure 3. Comparison between model prediction and experiments of BA polymerization rate [mol/l/s]; left: polymerization in bulk in the temperature range 80-130 °C; right: predicted and experimental polymerization rates in bulk and in xylene at 130°C.

The global sensitivity analysis performed on self-initiation, backbiting and β -scission (Fig. 4) shows that these three reactions are highly important for the correct description of the polymerization rate.

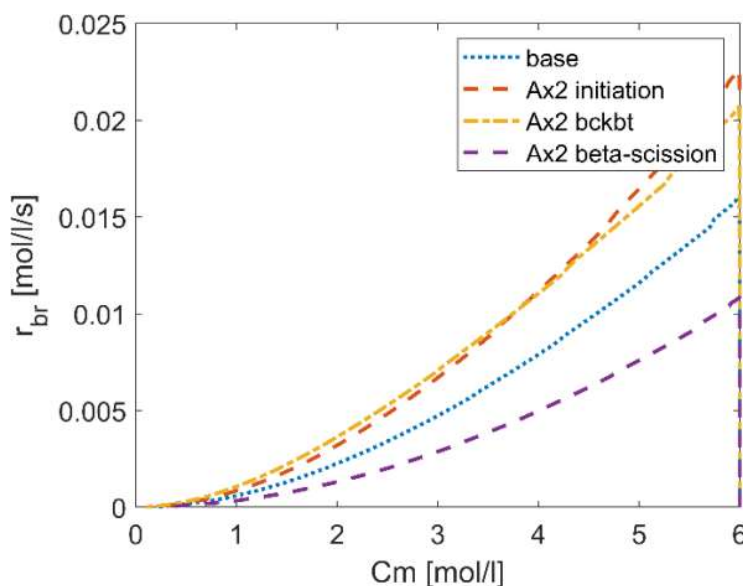


Figure 4. Global sensitivity analysis of polymerization rate [mol/l/s] against monomer concentration [mol/l] to thermal self-initiation, backbiting and β -scission reactions.

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