Kinetic Modeling of RAFT Polymerization via Dithiobenzoate Agents Considering the Missing Step Theory

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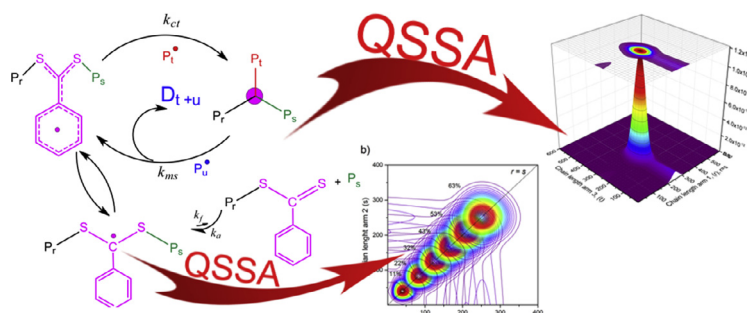[b] Centro de Investigación en Química Aplicada, Saltillo, Coah, Mexico
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HIGHLIGHTS

- First report on modeling of the Missing Step Theory in RAFT via dithiobenzoates.
- The model is able to predict the behavior of the 2-arm and 3-arm intermediates.
- Solution of very large dimension population balance equation system.
- Comparison of the Methyl Acrylate and Styrene experimental data and the model results.
- The QSSA of 3-arm intermediate species is strictly validated.

GRAPHICAL ABSTRACT

ABSTRACT

The reversible addition–fragmentation chain transfer (RAFT) polymerization via dithiobenzoates with reactivation of the 2-arm intermediates in the kinetic mechanism, proposed by Buback and Vana in the Missing Step theory, was modeled for first time via the Reduced Stiffness by Quasi Steady State Approximation (RSQSSA) methodology. The methyl acrylate (MA) and the styrene (Sty) polymerization were analyzed by a comparison of the theoretical solution with the experimental data collected in the literature. The Quasi-Steady State was valid for the 3-arm intermediates only when the kinetic rate constant of reactivation of these species was close to or above the values of the addition rate coefficient. For both MA and Sty polymerizations, the simulations demonstrated a good agreement between the model solutions and experimental values, in the evolution of conversion with time, M_n and M_w. Also, the full-molecular weight distribution predicted by the model indicated a very good match with the experimental data. A symmetric bivariate population of 2-arm intermediates was obtained, resulting in a high probability to find species with the same chain length in both arms. Similarly, the results showed that the 3-arm intermediates with the same chain length in each arm could be mostly generated, but in this case a no-symmetric multivariate population was found.

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1. Introduction

The dilemma related to the kinetic mechanism of the addition-fragmentation chain transfer (RAFT) polymerization using dithiobenzoates as RAFT agents, seems to be closed [1,2]. As it is known, the debate was principally focused in explaining the rate

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retardation seen in RAFT polymerizations [3] when using dithiobenzoates associated to the stability of the intermediate radical species (**3**) [4] and also to the structural effects of the resonance-stabilized radical intermediate, see Scheme 1.

A full picture of the debate is found in several reviews [4–6]. Three theories have been proposed to interpret this phenomenon: 1) the slow fragmentation (SF) hypothesis by Barner-Kowollik, 2) the intermediate radical termination (IRT) by Monteiro and De Brouwer, and 3) the intermediate radical termination with oligomers (IRTO) by Perrier and Konkolewicz.

The SF theory proposes a very slow fragmentation of the intermediate radicals **3**, which capture a couple of living chains (**1**) and produces a rate retardation. The polymerization mechanism keeps the original scheme of RAFT polymerization suggested by CSIRO, avoiding the side-reactions. The low values of the fragmentation rate constant ($k_f \approx 1 \times 10^{-2}\,s^{-1}$) produce a high stability of **3**, it gives rise to a build-up of the concentration of specie through the polymerization [7]. *Ab initio* calculations [8], spin trap experimental measurements [9] and experiments with thioketone agents [10] supported this theory, but the high concentration of **3** (as high as the concentration of the dormant species **2**) [11] predicted by SF is the main criticism of this hypothesis, since a low concentration of **3** was directly measured by electron spin resonance (EPR) [12].

The IRT theory assumes that **3** may irreversibly react with living radicals (**1**) and this step produces dead polymers known as 3-arm stars (**4**) [13]. This leads to a decrease of the concentration of the living radical and therefore retardation in the polymerization may be observed. The high instability of 3 predicts high fragmentation rate values ($k_f \approx 1 \times 10^4\,s^{-1}$), which have been recently estimated by new electron paramagnetic resonance (EPR) methods [14]. The concentration of **3** is in agreement with ESR measure-

ments and theoretical works support the IRT model [15,16]. The high values of the cross-termination rate constant required to decrease the polymerization rate, results in high concentration of **4**, which has not been seen in acrylate polymerizations. The discrimination method presented by Suzuki et al. [17] points out that the IRT theory predicts the experimental polymerization rate better than those obtained by SF theory in a miniemulsion polymerization. In this technique the bimolecular termination is suppressed, such as cross-termination, leading to increase the rate of polymerization with respect to bulk technique. IRT model can reflect this increasing in the reaction rate, but the SF model is almost insensitive to the change of reaction technique, resulting in almost the same polymerization rate as the bulk technique.

More recently, Perrier et al. [18] proposed another hypothesis (IRTO, intermediate radical termination with oligomers) that modifies the IRT model in an attempt to conciliate the theoretical predictions with the experimental observations. The fundament of IRTO is based in the steric hindrances provided by both long arms of **3**, avoiding a termination with long chains radicals **1** and expecting to have an effective reaction with small molecules able to diffuse near the active sites. In this model the cross-termination reaction is postulated to occur only between the intermediate radicals **3** and oligomeric (r = 1, 2) living radicals **1**, as shown in Scheme 1, thus one arm of species **5** is very short and the polymer molecules are mostly linear. IRTO theory is supported by a theoretical fit to experimental data [18], Brown et al. [19] have carried out a styrene polymerization using a fluorescent carbazole-RAFT agent, which exhibits the retardation effect. By a nickel desulfurization method, the S-C bonds were attacked and the macromolecule was fragmented: for the dormant species the polymeric chain is separated from the carbazole group, but in 3-arm star products
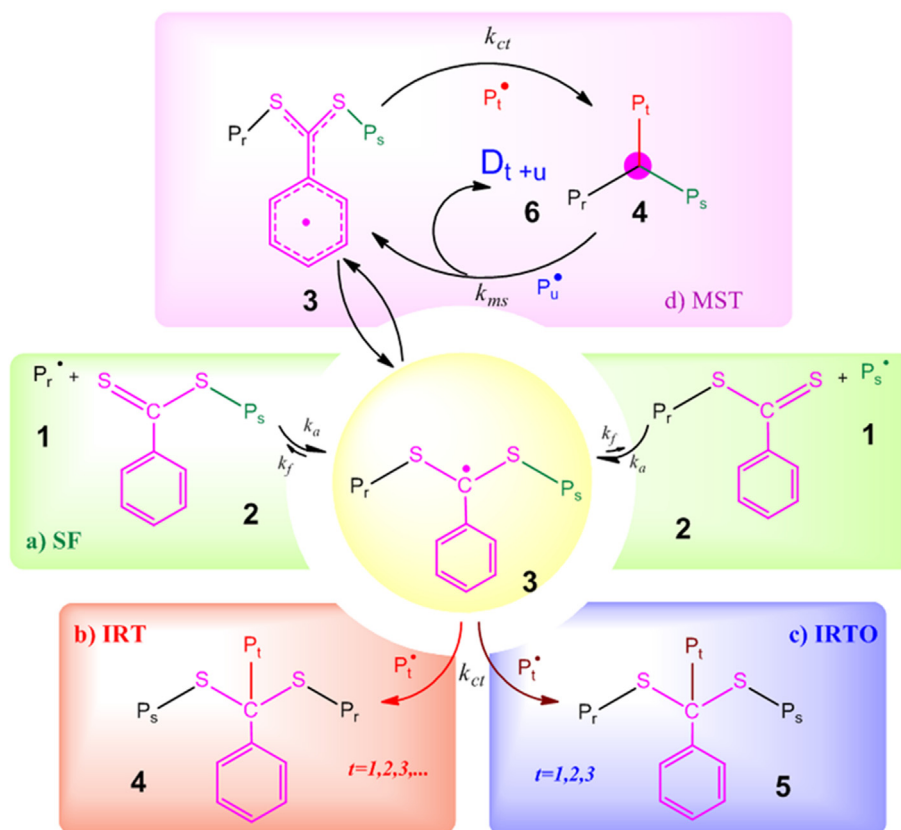
Scheme 1. Kinetic theories in RAFT polymerization using dithiobenzoates: a) Slow Fragmentation, b) Intermediate Radical Termination, c) Intermediate Radical Termination with Oligomers and d) Missing Step.