

Mathematical modeling of reverse atom transfer radical polymerization in miniemulsion

A. Zurman^a, C. Sarmoria^{a,b}, A. Brandolin^{a,b}, M. Asteasuain^{a,b,*}

^a Planta Piloto de Ingeniería Química (PLAPIQUI), CONICET-UNS, Camino La Carrindanga km 7, 8000 Bahía Blanca, Argentina

^b Departamento de Ingeniería Química, Universidad Nacional del Sur (UNS), Avda. Alem 1253, 8000 Bahía Blanca, Argentina

ARTICLE INFO

Article history:

Received 18 September 2017

Received in revised form 15 December 2017

Accepted 16 December 2017

Keywords:

Reverse atom transfer radical

polymerization

Miniemulsion

Water-soluble initiator

Molecular weight distribution

Mathematical modeling

ABSTRACT

In this work, we study the reverse atom transfer radical polymerization in miniemulsion using a water-soluble initiator. This study is motivated by the technological advantages of performing polymerizations in dispersed systems, and the attractive possibilities of controlled radical polymerization techniques to produce tailor made polymers. A mathematical model for this system is presented. The model predicts average molecular properties as well as the full molecular weight distribution (MWD) for different experimental conditions. The method of moments is applied for calculating average properties and the probability generating function (pgf) technique is used to model the MWD. The model is based on the mass balance equations of the reacting species. It takes into account the reactions in both the aqueous and organic phases and the mass transfer between them. Predicted conversions, average molecular weights, polydispersity indexes and MWDs for different experimental conditions agree well with experimental data reported in the literature.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Controlled radical polymerization (CRP) techniques have emerged as a promising field since they allow obtaining polymers with controlled molecular weights, low polydispersities, and defined architectures, employing mild reaction conditions. These techniques have been extensively studied in homogeneous systems, such as bulk and solution. However, over the last few years, there has been great interest in adapting these techniques to aqueous heterogeneous systems because they constitute a good alternative for large-scale production. The reasons are many: aqueous dispersed systems are environmentally friendly, show very good heat transfer, better process control, ease of mixing, flexibility, and ease of handling of the final product [1,2]. In fact, due to these advantages, many polymers currently obtained by conventional free-radical polymerization are produced in emulsion systems [1].

The application of CRP in dispersed systems has not been straightforward because it presents some complications, including partitioning of species between aqueous and organic phases, exit of radicals from polymer particles, poor colloidal stability, and interactions of species with other components of the recipe [1]. Despite these issues, different CRP techniques have been successfully

applied in dispersed systems for several monomers and at different experimental conditions [3].

The first attempts to adapt CRP to aqueous dispersed systems were in emulsion. They were mostly unsuccessful because the emulsions did not present enough colloidal stability and had mass transfer limitations. Further studies focused on miniemulsions, where there is no need of diffusion of reactants through the aqueous phase from monomer droplets to micelles, as in emulsion systems. Miniemulsions are also able to host the polymerization of highly water insoluble monomers and to form particles containing additives such as dyes or pigments. [2,4]. Nevertheless, an hydrophobe of low molecular weight may need to be removed from the final latex, something that constitutes a disadvantage [1].

Atom transfer radical polymerization (ATRP) is one of the more widespread CRP techniques, together with nitroxide-mediated polymerization (NMP) and reversible addition–fragmentation chain transfer polymerization (RAFT). ATRP presents some distinct advantages over the others, such as the wide range of monomers it can polymerize, the commercial availability of reagents, the mild temperatures it employs and the capability of obtaining end-functionalized chains for subsequent reactions [5].

ATRP is based on the reversible equilibrium of a small number of radicals (P_n^*) with a much larger number of dormant species ($P_n\text{Br}$) (Fig. 1). The dormant species react with a transition metal complex in its lower oxidation state (CuBr_1/L), which acts as an

* Corresponding author at: Planta Piloto de Ingeniería Química (PLAPIQUI), CONICET-UNS, Camino La Carrindanga km 7, 8000 Bahía Blanca, Argentina.

E-mail address: masteasuain@plapiqui.edu.ar (M. Asteasuain).

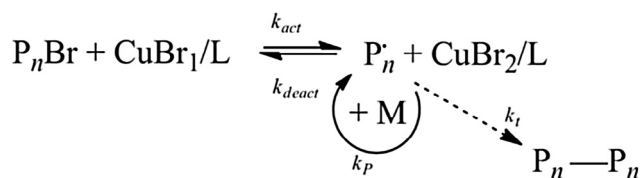


Fig. 1. Scheme of ATRP equilibrium.

activator, to produce the radicals and the transition metal complex in its higher oxidation state (CuBr_2/L), known as the deactivator. During this reaction, a halogen atom is transferred from the dormant species to the deactivator. The radicals may propagate incorporating more monomer units, terminate with other radicals or be deactivated again, regenerating the dormant species and the activator.

ATRP offers different procedures for initiating the reaction, as reported elsewhere [6]. One of these procedures is the reverse ATRP, in which the reaction begins with a conventional radical initiator (from which radicals P_n^\bullet are generated) and the transition metal complex in its higher oxidation state. This procedure works well in aqueous dispersed systems since it employs $\text{Cu}(\text{II})$ complexes that are more tolerant to air than the $\text{Cu}(\text{I})$ complexes employed in direct ATRP [4]. Besides, it can employ many of the initiators used in conventional free-radical polymerization. Despite some disadvantages, such as relatively low initiation efficiency, reverse ATRP has demonstrated to be robust enough for obtaining polymers with controlled molecular weights and narrow molecular weight distributions in miniemulsion systems [7–9].

ATRP in miniemulsion has been extensively studied [2]. Considerable experimental research has been carried out employing several monomers (i.e. styrene, butyl acrylate, butyl methacrylate), varying the initiating procedure, the recipe and other experimental conditions (i.e. initiator, ligand, surfactant) [7,10,8,11]. Furthermore, theoretical work has been reported, employing deterministic as well as stochastic methods. For instance, Zetterlund et al. [11–15] studied extensively the compartmentalization effect in ATRP in dispersed systems using the modified Smith–Ewart equations. In addition, they investigated the effects of the partitioning of activator and deactivator, employing the software package Predici. At about the same time, Cunningham et al. [16] studied compartmentalization effects on polymerization rate and livingness of the reaction using the modified Smith–Ewart equations for a different system. They presented results on an average number of radicals per particle that indicate the system behaved as a bulk one for particles sized over 100 nm. Kagawa et al. [13] observed this behavior for particles larger than 70 nm for a similar system. On the other hand, Tobita [17–19] performed Monte Carlo simulations of ATRP in miniemulsion. He studied the effect of particle diameter on the kinetics and the role of segregation and fluctuation effects that are implicit in compartmentalized systems.

The studies reported so far have focused on phenomena present in ATRP in miniemulsion, such as compartmentalization and partitioning of components between phases, as well as their causes and how to exploit them to improve the process performance. To the best of our knowledge, a mathematical model able to predict accurately the molecular weight distribution has not been developed for this system.

In the above context, this work aims at developing a mathematical tool to predict the main molecular properties of the product obtained through a reverse ATRP in miniemulsion using a water-soluble initiator. The user of this tool would be able to calculate the molecular characteristics of the final polymer, given a certain polymerization recipe. The model we present in this work predicts average molecular properties, such as number and weight average

molecular weights, as well as the full molecular weight distribution (MWD) for different experimental conditions. It is applicable to systems with particle sizes large enough for compartmentalization effects to be negligible. It is based on the mass balance equations of the reacting species. The method of moments was applied for calculating average properties and the probability generating function (pgf) technique is used to model the MWD. Parameter estimation was performed to fit the values of several model parameters, employing experimental data available in the literature [7].

2. Mathematical model

A mathematical model of the reverse ATRP in miniemulsion initiated by a water-soluble initiator is developed based on the mass balance equations of the reacting species. It takes into account the reactions in both the aqueous and organic phases, as well as the mass transfer between them.

2.1. Description of the heterogeneous system

In order to understand the mechanisms and phenomena involved, the system is described first.

The miniemulsion consists of an organic phase, composed of the monomer dispersed as droplets in a continuous aqueous phase. The monomer is also partially dissolved in the aqueous phase. The initial composition of the miniemulsion includes the water-soluble initiator present in the aqueous phase, and a deactivator dissolved in both the organic and aqueous phases. For the sake of clarity, CuBr_2/L will be taken as an example of a usual deactivator in the remainder of the paper without losing model generality. The distribution of the reacting species in the miniemulsion is shown in Fig. 2.

The water-soluble initiator decomposes in the aqueous phase, generating radicals. These radicals may react with other species present in the aqueous phase: with the monomer in the propagation reaction or the transfer to monomer reaction, with other radicals in termination reactions, or with deactivator CuBr_2/L . The latter reaction generates dormant species as well as the activator CuBr_1/L . The activator and the dormant species can react with each other in the reverse reaction, establishing the ATRP equilibrium in the water phase. If the radicals propagate, they grow until they reach a chain length that renders them hydrophobic, or surface-active. At the same time, dormant species also become hydrophobic when they reach a given chain length. It is considered that as soon as these species achieve hydrophobicity, they irreversibly enter the organic phase, where they may be deactivated (radicals)

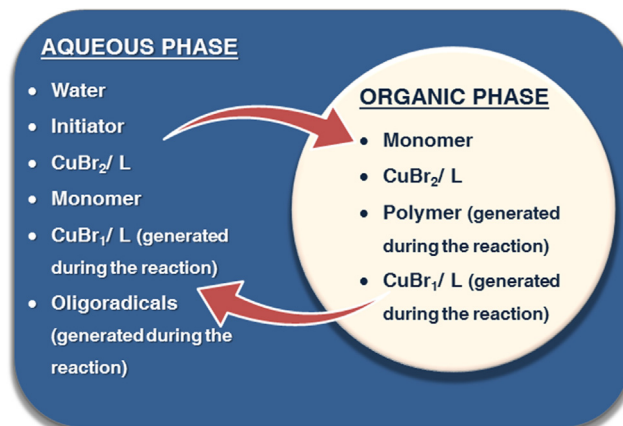


Fig. 2. Distribution of reacting species in the heterogeneous system.

Download English Version:

<https://daneshyari.com/en/article/7957911>

Download Persian Version:

<https://daneshyari.com/article/7957911>

[Daneshyari.com](https://daneshyari.com)