
KINETICS OF MICROEMULSION COPOLYMERIZATION OF STYRENE AND METHYL METHACRYLATE FOLLOWED BY CALORIMETRY

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1. Abstract

In this work the kinetics of microemulsion copolymerization of styrene and methyl methacrylate followed by calorimetry is presented. Microemulsion copolymerization kinetics usually is followed by gravimetry, however, it is an invasive technique because it is necessary to take out samples from the reactor. Furthermore it takes a long time to have conversion data. Calorimetry is a non-invasive technique which allows following on line the reaction. Reactions were carried out at 60 °C in a three neck reactor with a capacity of 500mL. A calorimetric probe was introduced to the reactor. Conversion curves obtained by calorimetry agree with those obtained by gravimetry. By calorimetry conversion can be followed *on line*.

2. Introduction

Microemulsion polymerization is a novel process for synthesizing in a routinely fashion latexes containing particles of nanosize scale (< 50 nm), each of which is composed of a few macromolecules of high molar mass (> 106 Dalton) [1, 2]. The potential applications of these colloidal polymers in medical, biological and industrial processes are enormous. However, for this process to be successful, it is necessary to increase polymer content by semicontinuous or continuous monomer addition [3, 4].

Microemulsion copolymerization is a complex heterogeneous process where transport of monomers, free radicals and other species between the aqueous and organic phases, take place. Compared with other heterogeneous polymerization processes (suspension or emulsion), microemulsion polymerization is a more complicated system. Kinetic and colloidal parameters are controlled by monomer partitioning between the phases, particle nucleation, and radicals adsorption and desorption [5, 6]. Copolymer properties depend on composition, sequence distribution and monomers' properties. Because monitoring copolymerization reactions permits adjusting composition through the reaction without the need to use complex kinetic models, it has been the focus of wide research, where different approaches have been employed. For example, gas chromatography has been used to follow on line conversion and composition in solution and emulsion polymerization and gravimetry,

however, this techniques are invasive since it is necessary to withdraw samples from the reactor [7].

Most of the techniques that are used for monitoring the kinetic of polymerization are invasive since it is necessary to take out samples from the reactor which could modify the reaction conditions. Calorimetry is a technique that can be used to follow the kinetics in continuous form and without taking out samples from the reactor.

The calorimetric method consists on following the quantity of released or absorbed energy needed to maintain constant the reaction temperature.

In this work we report the kinetics of O/W microemulsion copolymerization of methyl methacrylate (MMA) and styrene (St) using DTAB as surfactant. The kinetics were followed by calorimetry and the conversion curves were compared with data obtained by gravimetry.

3. Materials

DTAB (99%+ pure from Tokyo Kasei) was used as received. St and MMA were passed through a TR-7 or a HR-4 column (Scientific Polymer Products), respectively to remove the inhibitors. The initiator 2,2-azobis(2-amidinopropane) hydrochloride (V-50) from Wako Chem. was purified by recrystallization from methanol. Doubly distilled and de-ionized water was employed. Reactions were carried in Heat Flow & Power Compensation Calorimetry of HEL out at 60°C in 500-mL reactor. The reacting system was continuously stirred and sparged with argon throughout the reaction. The reactions were followed *on line* by a calorimetric probe introduced into the reactor.

Samples at different reaction times were taken to follow conversion by gravimetry. To stoop the reaction the samples were poured in hydroquinone solution (0.05M) and cooled. . Unreacted monomers and water were eliminated by evaporation under vacuum at 40 °C until constant weight.

4. Results and Discusión

Figure 1 shows a thermogram of the microemulsion copolymerization of MMA-St with a ratio of 75/25, where it can observed that initially a high amount of heat is necessary to take the reactor to the reaction temperature (60 °C). Then, the amount of energy decreases until a period of stabilization is obtained. When the monomers are added again an increment in the heat flow is observed due to the heating of the monomers to the reaction temperature, when the monomers reach reaction temperature the amount of heat is stabilized again. . When the

initiator is added, reaction starts and a negative peak can be observed because the reaction is exothermic and a lower amount of energy is needed to maintain constant temperature. When the peak comes back to the baseline, it is considered that reaction has been completed. The polymerization peak presents two reaction intervals which are characteristic of microemulsion polymerization [1,2].

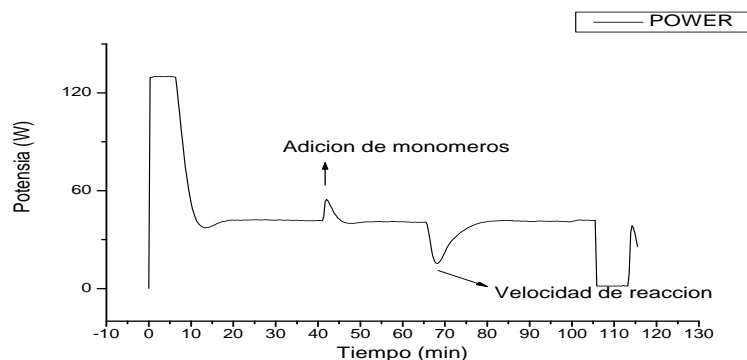


Figure 1. Thermogram of the microemulsion copolymerization of MMA-St/DTAB /Water system.

2.- Conversion as a function of time.

Conversion (X_{cal}) was determined by using the following equation:

$$X_{cal} = \left(1 - \frac{A}{A_t} \right) \quad (1)$$

where A is the cumulated area at time t and A_t is the final area and both values are related to the heat needed to maintain the reaction temperature when using the calorimeter. To follow a given reaction *on line* using calorimetry it is necessary to know the value of A_t before the reaction is monitored. In industrial production polymerizations are carried out under the same conditions and calorimetry can be a useful technique to control the reaction. In this case A_t can be determined by carrying out the reaction once under the same conditions and measuring the total area and final conversion by gravimetry.

Figure 2A, shows the conversions obtained in the copolymerization of MMA-St- with a ratio of 75/25, where it can be observed that there is a good agreement between calorimetry and gravimetry data. Similar results were obtained in the copolymerization of MMA-St when using ratios of 50/50 (Figure 2B) and 25/75 (Figure 2C). However, when using calorimetry there is the advantage that conversion can be obtained *on line* once the total heat of a given reaction is known.

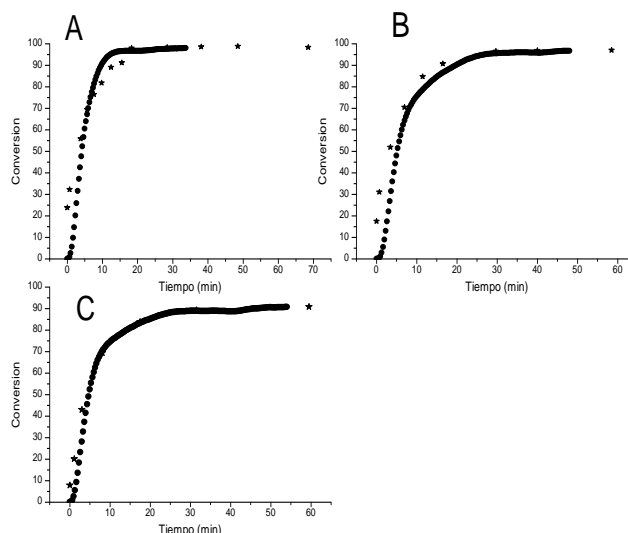


Figure 3 Comparison of conversion obtained by gravimetría (*) and calorimetría (!) in the microemulsion copolymerization of MMA-St with different ratios. (A) 75/25, (B) 50/50 and (C) 25/75.

5. Conclusions

There is a good concordance between conversion obtained by gravimetry and calorimetry. Calorimetry permits to monitor continuously conversion.

6. Bibliography.

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