

Estimation of conversion and copolymer composition in semicontinuous emulsion polymerization using calorimetric data

L. M. Gugliotta*, M. Arotçarena, J. R. Leiza and J. M. Asua†

Grupo de Ingeniería Química, Departamento de Química Aplicada, Facultad de Ciencias Químicas, Universidad del País Vasco, Apdo. 1072, 20080 San Sebastián, Spain

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A new approach to estimate conversion and copolymer composition in semicontinuous emulsion copolymerization systems based on calorimetric measurements was developed. The proposed approach was checked for two different monomer systems: butyl acrylate–styrene and vinyl acetate–butyl acrylate. The estimated values of conversion and copolymer composition obtained from calorimetric data were compared with measurements of conversion and cumulative copolymer composition by gravimetry, gas chromatography and ^1H n.m.r. A good agreement was achieved.

(Keywords: on-line estimation; copolymer composition; emulsion polymerization)

INTRODUCTION

In order to control a polymerization reaction process using a closed-loop control strategy, on-line measurements of the polymer properties or accurate estimates of these properties are necessary¹. During the last few decades considerable effort has been devoted to developing accurate and robust on-line devices for monitoring polymer properties². However, due to the physico-chemical nature of the polymerization systems, the development of on-line devices has been slower than in other chemical processes. The main drawbacks encountered in most of the on-line installations for emulsion polymerization systems reported in the open literature may be summarized as follows: (1) only discrete and delayed measurements of the polymer properties are obtained, and often the delayed measurements can make the implementation of control strategies difficult; and (2) most of the on-line devices cannot handle high solids content latexes, namely, latexes commonly used in industrial practice.

In several experimental set-ups for on-line monitoring of polymer composition in emulsion polymerization systems^{3–5} the reaction medium was continuously pumped through a circulation loop containing an injection valve that injected the sample into a gas chromatograph. Nevertheless, in order to avoid clogging and coagulation of the latex in the pump, injection valve and tubing the solids content should be lower than 30–35 wt%. To circumvent this difficulty Guyot *et al.*³, developed a sampling device which was fixed at the

bottom of the reactor and passed through the reactor wall. The range of solids content that could be handled by the equipment was not reported.

Alonso *et al.*⁶ and Ahmed and Mackey⁷ estimated the copolymer composition from on-line measurements of the reactor head-space vapour composition. This method is more robust and troublefree than those based on sampling the liquid reaction mixture. However, to obtain accurate measurements, thermodynamic equilibrium between the solid, liquid and vapour phases should be attained and the values of the monomer partition coefficients are required.

Recently, Leiza *et al.*⁸ have developed an automatic sampling system able to handle high solids content latexes (55 wt%). This apparatus has been used for on-line polymer composition control in the emulsion copolymerization of ethyl acrylate and methyl methacrylate⁹ and in the emulsion terpolymerization of vinyl acetate–methyl methacrylate–butyl acrylate¹⁰. In addition the experimental apparatus can be used for kinetic investigations of emulsion polymerization systems. The main drawback of this set-up is that only discrete and delayed measurements can be obtained.

Alternatively, the use of non-invasive sensors or instruments has emerged as a feasible and powerful tool for these purposes. Thus, ultrasonic velocity measurements and calorimetric measurements appear as promising continuous and accurate on-line measurement devices for emulsion polymerization systems. Hergeth *et al.*¹¹ and Hörning *et al.*¹² discussed the use of acoustic emissions to monitor emulsion homopolymerizations. More recently, Canegallo *et al.*¹³ reported the feasibility of using ultrasonic velocity measurements to monitor conversion in emulsion polymerization systems. The applicability of this technique to monitor emulsion copolymerization kinetics has yet to be proved technically.

*On leave from INTEC (Consejo Nacional de Investigaciones Científicas y Técnicas and Universidad Nacional del Litoral), Santa Fe, República Argentina

†To whom correspondence should be addressed

Reaction calorimetry offers the possibility of continuous and accurate on-line monitoring of polymerization reactions. The state of the art of isothermal bench scale calorimeters and their application to polymerization systems have been recently reviewed by Moritz¹⁴ and Schuler and Schmidt¹⁵. Moritz¹⁴ measured by calorimetry the polymerization rate in batch and semicontinuous emulsion homopolymerizations. Schuler and Schmidt¹⁵ reported that calorimetric state estimators may be used for polymerization reactor control and reactor state diagnosis and interpretation.

Urretabizkaia *et al.*¹⁶ proposed an approach to estimate conversion and copolymer composition in batch emulsion copolymerization using calorimetric data. A good agreement between copolymer composition based on on-line calorimetric measurements and that determined by off-line gas chromatographic measurements for three different monomer systems was reported. The main drawback of this approach is that the calculations have to be performed after the end of the process, namely, they cannot be carried out on-line. In addition, the extension of this approach to semicontinuous reactors is not evident. However, copolymer composition control requires on-line measurements and the use of semicontinuous reactors.

In the present work, a new approach for the on-line estimation of conversion and copolymer composition in batch and semicontinuous emulsion polymerization systems based on calorimetric data is presented.

EXPERIMENTAL

Semicontinuous emulsion polymerizations of butyl acrylate (BuA)-styrene (St) and vinyl acetate (VAc)-BuA were carried out at 60°C in a commercial reaction calorimeter (RC1, Mettler-Toledo) equipped with a stainless steel reactor (HP60 Mettler-Toledo). The recipes used in the experiments are given in Table 1. All materials were used as received.

Polymerizations were carried out as follows. The emulsifier and the buffer were dissolved in ~800 g of distilled and deionized (DDI) water, the initiator was dissolved in the remaining DDI water, and both solutions were added to the reactor. Then, the mixture of neat monomers was fed into the reactor at constant flow rate over 120 min. The evolution of the overall heat rate of polymerization, $Q_g(t)$, was measured. In addition, during the polymerization, samples were withdrawn from the reactor and the overall conversion and the copolymer composition were measured by gravimetry and by g.c., respectively. In some cases, the copolymer composition was also measured by ¹H n.m.r.

Table 1 Recipes used for the semicontinuous emulsion copolymerizations

Monomer system	BuA/St	VAc/BuA
Monomer ^a (g)	433	433
SLS (sodium lauryl sulfate) (g)	15	5
NaHCO ₃ (g)	5	2
K ₂ S ₂ O ₈ (g)	5	2
Distilled and deionized water (g)	867	867

^aMonomer molar ratios: BuA/St = 70/30 (L-1), BuA/St = 85/15 (L-2), VAc/BuA = 70/30 (L-3) and VAc/BuA = 50/50 (L-4)

MATHEMATICAL MODEL

The goal of the mathematical model is to estimate the overall conversion and the copolymer composition from the overall heat of polymerization, $Q_g(t)$, that is provided by the RC1 every 2 s. The overall heat rate of polymerization, $Q_g(t)$, depends on the polymerization rates as follows:

$$Q_g(t) = R_{pA}(-\Delta H_A) + R_{pB}(-\Delta H_B) \quad (1)$$

where R_{pA} and R_{pB} are the polymerization rates of monomers A and B, respectively, and $(-\Delta H_A)$ and $(-\Delta H_B)$ are the enthalpy of homopolymerization of the monomers. Notice that in equation (1) it is assumed that the enthalpy of cross-propagation is equal to the enthalpy of homopolymerization¹⁶.

Assuming that the extent of the aqueous phase polymerization is negligible, the polymerization rate of monomer i is:

$$R_{pi} = (k_{pAi}p_A + k_{pBi}p_B)[i]_p \frac{\bar{n}N_T}{N_A} \quad (2)$$

where k_{pij} is the propagation rate constant of monomer i with monomer j ($\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$), p_j the time averaged probability of finding a free radical with ultimate unit of type j in the polymer particles, $[i]_p$ the concentration of monomer i in the polymer particles (mol cm^{-3}), \bar{n} the average number of radicals per particle, N_T the total number of polymer particles and N_A the Avogadro number.

The probabilities are given by¹⁷:

$$p_j = \frac{k_{pj}[j]_p}{k_{pj}[j]_p + k_{pi}[i]_p} \quad (3)$$

$$p_i = 1 - p_j \quad (4)$$

The concentration of monomers in the polymer particles can be easily calculated using the equilibrium equations and the overall material balances by means of an iterative algorithm inspired by the method proposed by Omi *et al.*¹⁸ and successfully applied by Urretabizkaia and Asua¹⁹. In this work, the equilibrium equations were written in terms of partition coefficients as follows:

$$k_{j,k}^i = \frac{[i]_j}{[i]_k} \quad (5)$$

where $k_{j,k}^i$ is the partition coefficient of monomer i between phases j and k ; and $[i]_j$ and $[i]_k$ are the concentrations of monomer i in phases j and k , respectively. The partition coefficients can be obtained from the literature or from independent measurements.

Equations (1) and (2) can be used to obtain the unknown value of $\bar{n}N_T$ as follows:

$$\bar{n}N_T = \frac{Q_g(t)N_A}{(k_{pA1}p_A + k_{pBA}p_B)[A]_p(-\Delta H_A) + (k_{pAB}p_A + k_{pBB}p_B)[B]_p(-\Delta H_B)} \quad (6)$$

This value can be calculated every 2 s using the value of $Q_g(t)$ given by the RC1 and the values of the concentrations of monomers in the polymer particles as explained above.

Using the value of $\bar{n}N_T$, the amount of unreacted monomer in the reactor can be easily calculated by

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