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

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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 ^{1}H 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 necessary[1]. During the last few decades considerable effort has been devoted to developing accurate and robust on-line devices for monitoring polymer properties[2]. However, due to the physicochemical 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 Mackey[7] 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 methacrylate[9] and in the emulsion terpolymerization of vinyl acetate–methyl methacrylate–butyl acrylate[10]. 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.

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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 Moritz[14] and Schuler and Schmidt[15]. Moritz[14] measured by calorimetry the polymerization rate in batch and semicontinuous emulsion homopolymerizations. Schuler and Schmidt[15] 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 ^{1}H 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
$K_2S_2O_8$ (g)	5	2
Distilled and deionized water (g)	867	867

[a] Monomer 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:

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

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 homopolymerization[16].

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

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

where k_{pij} is the propagation rate constant of monomer i with monomer j (cm^3 mol^{-1} 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 by[17]:

$$p_j = \frac{k_{p_{ij}}[j]_p}{k_{p_{ij}}[j]_p + k_{p_{ji}}[i]_p} \tag{3}$$

$$p_i = 1 - p_j \tag{4}$$

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 Asua[19]. In this work, the equilibrium equations were written in terms of partition coefficients as follows:

$$k^i_{j,k} = \frac{[i]_j}{[i]_k} \tag{5}$$

where $k^i_{j,k}$ 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:

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

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

Table 2 Values of the parameters used in the estimation of the conversion and cumulative copolymer composition from calorimetric measurements

r_{12}, r_{21} (ref. 20)		0.2		0.75
r_{13}, r_{31} (ref. 16)		6.36		0.037
k_{p11} (ref. 21), k_{p22} (ref. 20), k_{p33} (ref. 21) (cm^3 mol^{-1} s^{-1})	0.151×10^6		0.343×10^6	0.235×10^7
$k_{p.w}{}^1$, $k_{d.w}{}^1$ (ref. 22)		480		740
$k_{p.w}{}^2$, $k_{d.w}{}^2$ (ref. 22)		1080		1810
$k_{p.w}{}^3$, $k_{d.w}{}^3$ (ref. 22)		31		37
$(-\Delta H_1)$, $(-\Delta H_2)$, $(-\Delta H_3)$ (J mol^{-1}) (ref. 23)	78×10^3		74×10^3	89.5×10^3

1, BuA; 2, St, 3, VAc
p, polymer particles phase; w, aqueous phase; d, monomer droplets phase

integrating the material balances for the monomers given by the following equation:

$$\frac{\mathrm{d}i}{\mathrm{d}t} = -(k_{p_{ii}}p_i + k_{p_{ji}}p_j)[i]_p\frac{\bar{n}N_T}{N_A} + F_i; \quad i,j = \mathrm{A,B}; \quad i \neq j \tag{7}$$

where F_i is the feed flow rate of monomer i (mol s^{-1}).

The fractional conversions $X_i(t)$ are:

$$X_i(t) = \frac{M_i(t) - i(t)}{M_i(t)} \tag{8}$$

with

$$M_i(t) = M_{i0} + \int_0^t F_i\,\mathrm{d}t; \quad i = \mathrm{A,B} \tag{9}$$

where $i(t)$ is the number of unreacted moles of monomer i (mol) in the reactor at time t, and M_{i0} is the initial number of moles of monomer i in the reactor (mol).

The overall gravimetric conversion is given by:

$$X_g(t) = \frac{X_A(t)M_A(t)M_{WA} + X_B(t)M_B(t)M_{WB}}{M_{AT}M_{WA} + M_{BT}M_{WB}} \tag{10}$$

where M_{AT} and M_{BT} are the total amount of moles of monomers A and B to be added into the reactor at the end of polymerization and M_{WA} and M_{WB} the molecular weights of monomer A and B, respectively.

The cumulative copolymer composition could also be calculated in each integration step by means of the following equation:

$$Y_A = \frac{M_A(t) - A(t)}{M_A(t) - A(t) + M_B(t) - B(t)} \tag{11}$$

The values of the propagation rate constants, enthalpy of homopolymerization, monomer reactivity ratios and monomer partition coefficients used in this work are given in *Table 2*.

RESULTS AND DISCUSSION

Figure 1a presents the comparison between the estimated and experimental overall gravimetric conversions (calculated from gravimetric and chromatographic measurements) for the semicontinuous emulsion copolymerization of BuA/St = 70/30 (run L-1). It can be seen that a good agreement between the estimated and experimental conversions is obtained during the whole experiment.

In *Figure 1b* a comparison between the cumulative copolymer composition estimated from the calorimetric data and that calculated from g.c. measurements is presented. It can be seen that the cumulative copolymer composition estimated from the calorimetric data is in agreement with that obtained from g.c. measurements.

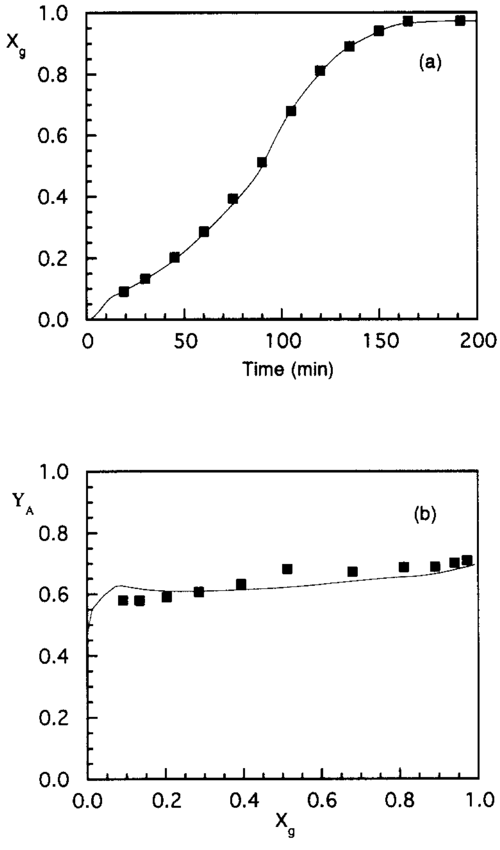

Figure 1 Semicontinuous emulsion polymerization of BuA and St (run L-1 = 70/30). (a) Time evolution of the overall conversion: (——) estimated from calorimetric data; (■) calculated from gravimetric measurements. (b) Evolution of the cumulative copolymer composition: (——) estimated from calorimetric data; (■) calculated from gravimetric and g.c. measurements

Figures 2a and *b* show the evolution of the overall conversion and the cumulative copolymer composition for run L-2 (BuA/St = 85/15) calculated using the present approach and the values obtained off-line by gravimetry, g.c. and ^{1}H n.m.r. It can be seen that the agreement is even better than in the previous experiment.

Although the mixture of St and BuA was added into the reactor at a feed rate greater than that required to bring the process under starved conditions, the cumulative copolymer compositions obtained for the BuA/St system did not show a remarkable composition drift due to the relatively small difference between the reactivity ratios of BuA and St ($r_{BuA} = 0.2$ and $r_{St} = 0.75$). In order to check

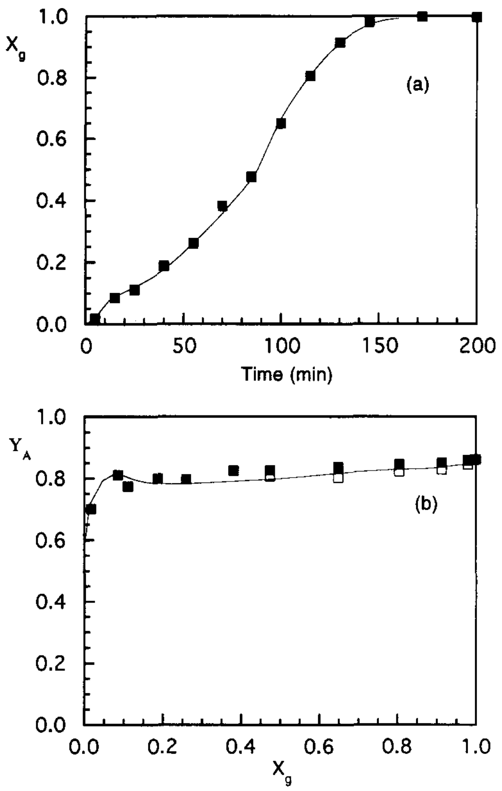

Figure 2 Semicontinuous emulsion polymerization of BuA and St (run L-2 = 85/15). (a) Time evolution of the overall conversion: (——) estimated from calorimetric data; (■) calculated from gravimetric measurements. (b) Evolution of the cumulative copolymer composition: (——) estimated from calorimetric data; (■) calculated from gravimetric and g.c. measurements; (□) measured by ^{1}H n.m.r.

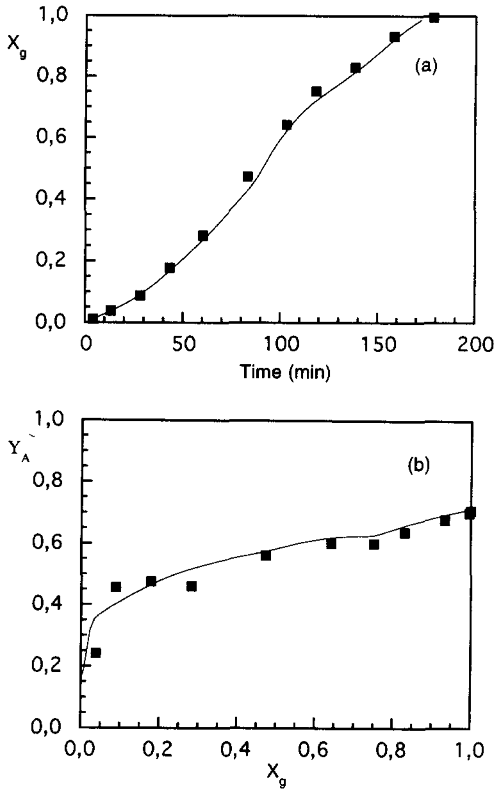

Figure 3 Semicontinuous emulsion polymerization of VAc and BuA (run L-3 = 70/30). (a) Time evolution of the overall conversion: (——) estimated from calorimetric data; (■) calculated from gravimetric measurements. (b) Evolution of the cumulative copolymer composition: (——) estimated from calorimetric data; (■) calculated from gravimetric and g.c. measurements

the approach under conditions in which a greater compositional drift is produced, a system with widely different reactivity ratios was chosen: VAc–BuA (r_{VAc} = 0.037 and r_{BuA} = 6.36).

Figures 3a and *b* present the evolution of the overall conversion and the cumulative copolymer composition estimated by means of the proposed approach and calculated from gravimetric and g.c. measurements for the semicontinuous emulsion copolymerization of VAc/BuA molar ratio = 70/30 (run L-3). It can be seen that in this monomer system the compositional drift is greater than for the St–BuA system. *Figures 3a* and *b* show that an excellent agreement between the values estimated from calorimetric measurements and those calculated from gravimetric and g.c. measurements was achieved.

A second monomer molar ratio (50/50) was studied for the VAc–BuA system, and the results obtained in this polymerization (run L-4) are plotted in *Figures 4a* and *b*. A good agreement was obtained for the overall conversion and cumulative copolymer composition calculated by the two methods.

CONCLUSIONS

A new approach to estimate on-line the conversion and the cumulative copolymer composition in batch and semicontinuous emulsion polymerization based on calorimetric measurements was developed. The approach uses a simple mathematical model of the semicontinuous

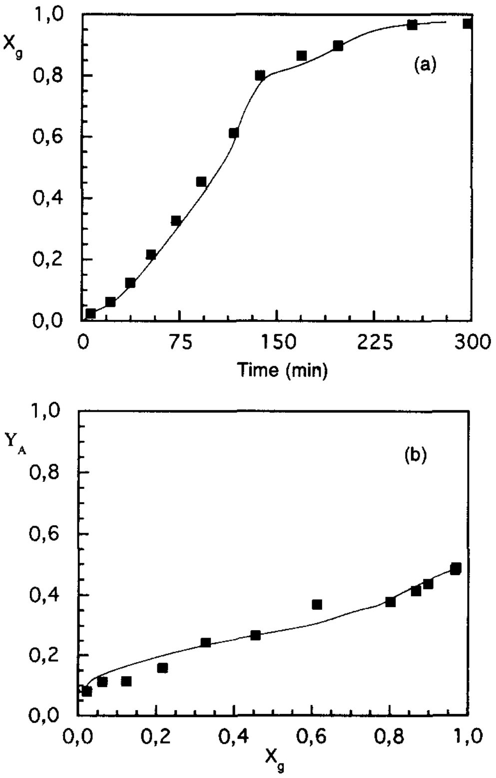

Figure 4 Semicontinuous emulsion polymerization of VAc and BuA (run L-4 = 50/50). (a) Time evolution of the overall conversion: (——) estimated from calorimetric data; (■) calculated from gravimetric measurements. (b) Evolution of the cumulative copolymer composition: (——) estimated from calorimetric data; (■) calculated from gravimetric and g.c. measurements

emulsion polymerization containing four parameters that have to be known previously: reactivity ratios, monomer partition coefficients, propagation rate constants and enthalpy of homopolymerization of each monomer involved. The method was validated for two different monomer systems (BuA–St and VAc–BuA). Two semicontinuous emulsion polymerizations were carried out with each monomer system. A good agreement was obtained between the values of conversion and cumulative copolymer composition estimated from calorimetric data and those obtained from gravimetry, g.c. and in some cases by ^{1}H n.m.r. It is worth mentioning that the approach could be useful to implement closed-loop copolymer composition control strategies.

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REFERENCES

1 MacGregor, J. F., Penlidis, A. and Hamielec, A. E. *Polym. Proc. Eng.* 1984, **2**, 179

2 Chien, D. H. C. and Penlidis, A. *Macromol. Chem. Phys.* 1990, **C30**(1), 1

3 Guyot, A., Guillot, J., Pichot, C. and Rios Guerrero, L. R. *Am. Chem. Soc. Symp. Ser.* 1981, **165**, 141

4 Dimitratos, Y. N. *PhD Dissertation*, Lehigh University, 1989

5 Van Doremaele, G. H. J. *PhD Dissertation*, Eindhoven Technische Universiteit, 1990

6 Alonso, M., Recasens, F. and Puigjaner, L. *Chem. Eng. Sci.* 1986, **41**(4), 1039

7 Ahmed, M. J. and Mackey, D. E. *Am. Chem. Soc. Symp. Ser.* 1989, **404**, 296

8 Leiza, J. R., de la Cal, J. C., Montes, M. and Asua, J. M. *Process Control Qual.* 1993, **4**, 197

9 Leiza, J. R., de la Cal, J. C., Meira, G. R. and Asua, J. M. *Polym. React. Eng.* 1992-93, **1**(4), 461

10 Urretabizkaia, A., Leiza, J. R. and Asua, J. M. *AIChE J.* 1994, **40**, 1850

11 Hergeth, W. D., Wartewig, S., Ranachowski, Z., Rzeszotarska, J. and Ranachowski, J. *Acta Polym.* 1988, **39**, 677

12 Hörning, K., Hergeth, W. D. and Wartewig, S. *Acta Polym.* 1989, **40**, 257

13 Canegallo, S., Apostolo, M., Morbidelli, M. and Storti, G. Third International Symposium on Radical Copolymers in Dispersed Media, Lyon, 1994

14 Moritz, H. U. in 'Polymer Reaction Engineering' (Eds K. H. Reichert and W. Geiseler), V.C.H. Verlag, Weinheim, 1989, p. 248

15 Schuler, H. and Schmidt, C. U. *Chem. Eng. Sci.* 1992, **47**(4), 899

16 Urretabizkaia, A., Sudol, E. D., El-Aasser, M. S. and Asua, J. M. *J. Polym. Sci., Polym. Chem. Edn* 1993, **31**, 2907

17 Forcada, J. and Asua, J. M. *J. Polym. Sci., Polym. Chem. Edn* 1985, **23**, 1955

18 Omi, S., Kushibiki, K., Negishi, M. and Iso, M. *Zairyo Gijutsu* 1985, **3**, 426

19 Urretabizkaia, A. and Asua, J. M. *J. Polym. Sci., Polym. Chem. Edn* 1994, **32**, 1761

20 de la Cal, J. C., Echevarria, A., Meira, G. R. and Asua, J. M. *J. Appl. Polym. Sci.* submitted

21 Delgado, J. *PhD Dissertation*, Lehigh University, 1986

22 Gugliotta, L. M., Arzamendi, G. and Asua, J. M. *J. Appl. Polym. Sci.* in press

23 Brandrup, J. and Immergut, E. H. (Eds) 'Polymer Handbook', 2nd Edn, Wiley, New York, 1989