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Dynamic optimization of non-linear emulsion copolymerization systems Open-loop control of composition and molecular weight distribution

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Abstract

Time optimal monomer and chain-transfer agent feed profiles were computed and implemented experimentally for the simultaneous control of copolymer composition and molecular weight distribution in non-linear emulsion copolymerization systems. Iterative dynamic programming was used for the off-line calculation of the optimal feed policies. This approach can deal with constrained optimization of systems described by complex mathematical models, as those needed for the emulsion copolymerization kinetics, especially when the computation of the whole molecular weight distribution is included. The proposed approach was applied to the semibatch methylmethacrylate (MMA)/*n*-butylacrylate (*n*-BA) emulsion copolymerization, using *n*-dodecanethiol as chain-transfer agent, and allowed the production of copolymers with constant composition and with well-defined molecular weight distributions. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Optimization; Iterative dynamic programming; Emulsion polymerization; MWD; Copolymer composition; MMA/*n*-BA; Chain-transfer agent

1. Introduction

Emulsion polymerization is currently the predominant process used in industry to produce a great variety of polymers of multiple uses (e.g. paints, adhesives, coatings, varnishes, carpet backings and binders). Many applications of these polymer latexes require the formation of a continuous film with high mechanical strength. Both the film formation process and the mechanical properties of the film strongly depend on the chemical composition and molecular weight distribution (MWD) of the polymer. Chemical composition mainly determines the glass transition temperature (T_g) of a copolymer [1]. On the other hand, MWD affects important end-use properties of the film such as adhesion, elasticity, strength, toughness, and solvent resistance. Thus, polymer chains of high molecular weight provide mechanical resistance and polymer chains of low molecular weight impart compatibility and adhesion. Latexes having a proper balance of high and low molecular weight polymers have been reported to be particularly useful for contact adhesives [2–4]. It is worth mentioning that for these systems the average molecular weights can be misleading. Therefore, there is a strong incentive to develop strategies to control copolymer composition and the complete MWD of polymer latexes.

In order to allow the closed-loop control of the composition and MWD, these properties should be measured or at least on-line inferred. On-line estimation of copolymer composition have frequently been reported in literature based on measurement obtained from different sensors (gas chromatography, calorimetry, and Raman, NIR and MIR spectroscopies among others) [5]. However, the on-line measurement and/or estimation of the MWD in emulsion polymerization systems is still an unsolved issue. Thus, the on-line measurement of the MWD by SEC is rather time consuming and virtually impossible in emulsion polymerization reactions (due to problems associated with sample preparation). In addition, the compartmentalized nature of the emulsion polymerization, generally speaking, makes the MWD non-observable from typically available on-line measurements (monomer conversion and temperatures). Nevertheless, under some conditions of practical significance, the MWD of emulsion polymers is not affected by the compartmentalization of the system. A typical example is when a chain-transfer agent is used and the kinetic chain length is controlled by the chain-transfer reaction to CTA

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in linear polymer systems. Under these circumstances the MWD of the polymer can be on-line inferred by means of open-loop observers [6–9] because the instantaneous MWD is only a function of the unreacted monomer/CTA ratio in the polymer particles, and the instantaneous polydispersity of the polymer produced is equal to 2.

More generally, multirate state observers (MSO) have been proposed for the on-line estimation of the MWD. MSO can be used to combine fast and frequent measurements (for instance, temperature and monomer concentrations) with delayed and infrequent measurements (for instance, the MWD obtained by size exclusion chromatography (SEC)) for control purposes. MSO were applied to solution polymerization of styrene [10] and MMA [11–15]. For emulsion polymerization, Mutha et al. [16] showed that an MSO based on a fixed-lag extended Kalman filter estimator exhibited generally a good convergence to the true states and robustness to measurement and process noise. The proposed estimator was capable of handling systems where measurement delay was very long by using multiple sets of measurement devices or taking more frequent measurements. The estimator was validated by simulation in the batch emulsion copolymerization of acrylonitrile/butadiene using as frequent measurements of the density and slow measurements of copolymer composition, average particle size and polymer viscosity to determine the average molecular weights. The estimator provided estimates of conversion, copolymer composition, particle number, average number of radicals in the polymer particles and number-average molecular weight, but unfortunately the estimation of the entire MWD was not reported. In addition, the off-line measurements are rather labor intensive.

It is worth noting the differences between linear and non-linear polymers. Linear polymers are those which are formed in a polymerization where inactive polymer chains, once produced, do not suffer any reaction that modifies their structure. If chain-transfer agents (CTA) are used so that the chain transfer to the CTA is the main chain termination event, the instantaneous MWD of linear polymers can be inferred on-line from the amounts of unreacted monomers and CTA [6,7]. In addition, the desired MWD can be built as the sum of instantaneous MWDs produced along the polymerization process [7]. Based on these ideas, the on-line control of the MWD of polystyrene latexes using different CTAs [6–8] and the simultaneous on-line control of copolymer composition and MWD (narrow, bimodal and broad distributions) of styrene/*n*-butyl acrylate latexes [9] have been achieved.

Non-linear (or branched) polymers [1] are those in which there are side branches or linked monomer molecules protruding from various central branch points along the main polymer chain. The branched polymer can be comb-like in structure with either long or short branches. When there is extensive branching, the polymer can have a dendritic structure in which there are branches protruding from other branches. If branched polymer chains can be linked to other similar branched polymer chains, the polymer formed is known as a cross-linked polymer. Branching in radical polymerization might occur if one of the following mechanisms is significant during the polymerization: (i) chain transfer to polymer, (ii) propagation to terminal double bond, (iii) β scission and/or (iv) divinylic monomers are used.

In these systems, inactive polymer chains can be reactivated by any of the above mentioned mechanisms modifying their structure (molecular weight), and hence the desired MWD cannot be decomposed in a series of instantaneous MWDs produced throughout the process. Therefore, control strategies as those developed for linear systems [6–9] cannot be used for non-linear polymers as it was recently demonstrated by Vicente et al. [17] for the methyl methacrylate/*n*-butyl acrylate (MMA/*n*-BA) copolymerization. The off-line measurement of the MWD of non-linear emulsion polymers might take several hours (solvent extraction might be necessary if gel is present) precluding the use of MSO [16]. Furthermore, the on-line estimation of the MWD of non-linear polymers is an unsolved issue, and hence the implementation in real-time of closed-loop strategies for controlling the MWD of non-linear polymers cannot be currently envisaged.

Under these circumstances, open-loop control offers a pragmatic alternative. The time varying control variables to be implemented in the open-loop strategy can be calculated through process optimization using a mathematical model for the emulsion polymerization system. It is worth pointing out that the success of the open-loop strategy relies on the goodness of the mathematical model and the absence (minimization) of unmodeled process disturbances. In this work the simultaneous control of the MWD and copolymer composition in the emulsion copolymerization of MMA and *n*-BA was considered. In this copolymerization, extensive chain transfer to polymer occurs leading to non-linear polymers.

The goal of the present work was the controlled production of MMA/*n*-BA copolymers with homogeneous compositions (50/50 in molar basis) and with well-defined final MWD (unimodal and bimodal MWD) by means of an open-loop control strategy. The copolymers considered were: (i) a copolymer of homogeneous composition 50/50 and final bimodal MWD with $\bar{M}_{w1} = 8.5 \times 10^5$, $PI_1 = 12$ and $\bar{M}_{w2} = 2 \times 10^4$, $PI_2 = 4$ and (ii) a copolymer of homogeneous composition 50/50 and unimodal MWD ($\bar{M}_w = 3.5 \times 10^5$ and $PI = 14$). This time optimal trajectories were validated in real-time experiments.

The optimal feed trajectories for monomers and CTA were computed by means of the Iterative Dynamic Programming, IDP [18–20]. This approach presents the advantage of being able to handle constrained optimization of systems described by complex mathematical models, as those needed for non-linear emulsion copolymerization systems. The mathematical model developed by Sayer [21] and validated with data gathered in the emulsion polymerization of MMA and *n*-BA [22,23] was used in the optimization. The polymerization mechanisms considered by the model include initiation, propagation, chain transfer to monomer, CTA and polymer, and termination by disproportionation. MWDs were computed by the adaptive orthogonal collocation technique presented by Pinto and Biscaia [24] and modified by Nele et al. [25]. A complete description of the mathematical model, including kinetic parameters, and the adaptive orthogonal collocation procedure [24,25] used to solve the MWD balance equations can be found elsewhere [21].

The manuscript is organized as follows: firstly the two cases considered in the dynamic optimization and the optimal addition profiles of the monomers and CTA obtained in the optimization are presented. Secondly, an open-loop control strategy based on the calculated optimal addition profiles was experimentally implemented.

2. Dynamic optimization

In this work the production of copolymers with homogeneous copolymer compositions (50/50 in molar basis) and well-defined MWD of the final copolymer was considered for dynamic optimization [26]. The optimization goals were included in the following objective function:

$$F = p_1 \sum_{i=1}^{ni} \left[\frac{y(i) - y(i)_{\mathrm{d}}}{y(i)_{\mathrm{d}}} \right]^2 + p_2 \sum_{k=1}^{10} \left[\frac{F_k{}^{\mathrm{f}} - F_{k\mathrm{d}}^{\mathrm{f}}}{F_{k\mathrm{d}}^{\mathrm{f}}} \right]^2 + p_3 \left[\frac{Q_{n-\mathrm{BA}}^{\mathrm{f}} - Q_{n-\mathrm{BAd}}^{\mathrm{f}}}{Q_{n-\mathrm{BAd}}^{\mathrm{f}}} \right]^2 + p_4 \left[\frac{Q_{\mathrm{MMA}}^{\mathrm{f}} - Q_{\mathrm{MMAd}}^{\mathrm{f}}}{Q_{\mathrm{MMAd}}^{\mathrm{f}}} \right]^2 \qquad (1)$$

where the first term of the right-hand side member compares the deviations in the copolymer composition along the process; the second term accounts for the differences between selected points (10 in this work) of the calculated ($F_k = \mathrm{d}W_{\mathrm{f}}/\mathrm{d}\,\mathrm{Log}(M)$) and desired ($F_{k\mathrm{d}}$) MWDs; the last two terms compare the amounts of monomers actually fed into the reactor, $Q_{n-\mathrm{BA}}^{\mathrm{f}}$ and $Q_{\mathrm{MMA}}^{\mathrm{f}}$, with those in the formulation, $Q_{n-\mathrm{BAd}}^{\mathrm{f}}$ and $Q_{\mathrm{MMAd}}^{\mathrm{f}}$, namely, they account for the solids content of the latex. The values assigned to the penalty functions were $p_1 = 8$, $p_2 = 2$ and $p_3 = p_4 = 40$ [26].

To allow the control of composition and MWD, three feed streams were used:

1. In the first stream, the less reactive monomer was fed (in this case, *n*-BA).
2. The second stream was a pre-emulsion containing most of the more reactive monomer (MMA) and part of the emulsifier.
3. The third stream was a pre-emulsion of CTA and a small amount of MMA. This was done to help the CTA to reach the polymerization loci, namely, to try to avoid diffusional limitations of the CTA.

The following two copolymers were considered:

C1 copolymer with a homogeneous copolymer composition MMA/*n*-BA = 50/50 and a bimodal MWD: $\bar{M}_{\mathrm{w}1} = 8.5 \times 10^5$ and $\mathrm{PI}_1 = 12$; $\bar{M}_{\mathrm{w}2} = 2 \times 10^4$ and $\mathrm{PI}_2 = 4$.

C2 copolymer with a homogeneous copolymer composition MMA/*n*-BA = 50/50 and a unimodal MWD: $\bar{M}_{\mathrm{w}} = 3.5 \times 10^5$ and PI = 14.

2.1. Case C1

Table 1 presents the formulation used in Case C1. Fig. 1 presents the optimum feed profiles obtained for this case. It can be seen that CTA was barely fed during the first half of the process (Fig. 1c) to initially produce the high molecular weight polymer fraction. Afterwards, the CTA feed rates were increased to produce the lower molecular weight polymer fractions. Simultaneously, in order to assure the production of a copolymer with the desired molecular weight and constant copolymer composition, Feeds 1 and 2 were fed more slowly during the second half of the process.

Fig. 2 shows the copolymer that, according to the model, will be obtained tracking the simulated optimum feed rates of Fig. 1. It can be seen that the desired copolymer composition (Fig. 2a) and final MWD (Fig. 2b) were not exactly achieved. These deviations were due to the multivariable nature of the objective function (Eq. (1)). Under these circumstances, the optimization solution was a compromise between the properties considered: copolymer composition, MWD and solids content.

2.2. Case C2

The second case (Table 2) considered was the production of a MMA/*n*-BA copolymer with a 50/50 homogeneous copolymer composition and an unimodal MWD ($\bar{M}_{\mathrm{w}} = 3.5 \times 10^5$ and PI = 14).

Fig. 3 presents the computed optimal feed rate profiles for this case. Fig. 3c shows that Feed 3, containing CTA, water, emulsifier and a small part of the MMA, was fed mainly at the beginning of the reaction while Feed 2, containing the remaining amount of MMA, was fed mainly at the second half of the reaction (Fig. 3b). This allowed the decoupling of the composition and MWD control problems, assuring the production of copolymer with constant composition.

Fig. 4 shows the copolymer that, according to the model, will be obtained tracking the simulated optimum feed rates of Fig. 3. As Case C2 aimed at the production of a copolymer with constant composition and a rather simple unimodal MWD (Fig. 4b) the process time was shorter than Case C1 (77 min vs 99 min). Therefore, productivity was significantly enhanced. Fig. 4 also shows that, in addition to the shorter process time, the polymer obtained in Case C2 was very close to the desired polymer.

Table 1
Formulation of the seeded emulsion copolymerization, Case C1 (80 °C, 200 rpm, feed time = 90 min)

	Initial charge	Feed 1	Feed 2	Feed 3
MMA (g)	–	–	123.85	59.00
n-BA (g)	–	234.30	–	–
AA (g)	–	2.34	1.24	0.59
CTA: *n*-dodecanethiol (g)	–	–	–	2.91
Water (g)	650.00	–	95.50	45.60
Emulsifier: Alipal CO-436 (g)	0.4	–	1.09	0.51
Initiator: $K_2S_2O_8$ (g)	1.50	–	–	–
Buffer: $NaHCO_3$ (g)	1.50	–	–	–
Seeds[a] (g)	150.0	–	–	–

[a] $N_{\text{pseed}} = 1 \times 10^{17}$ particles.

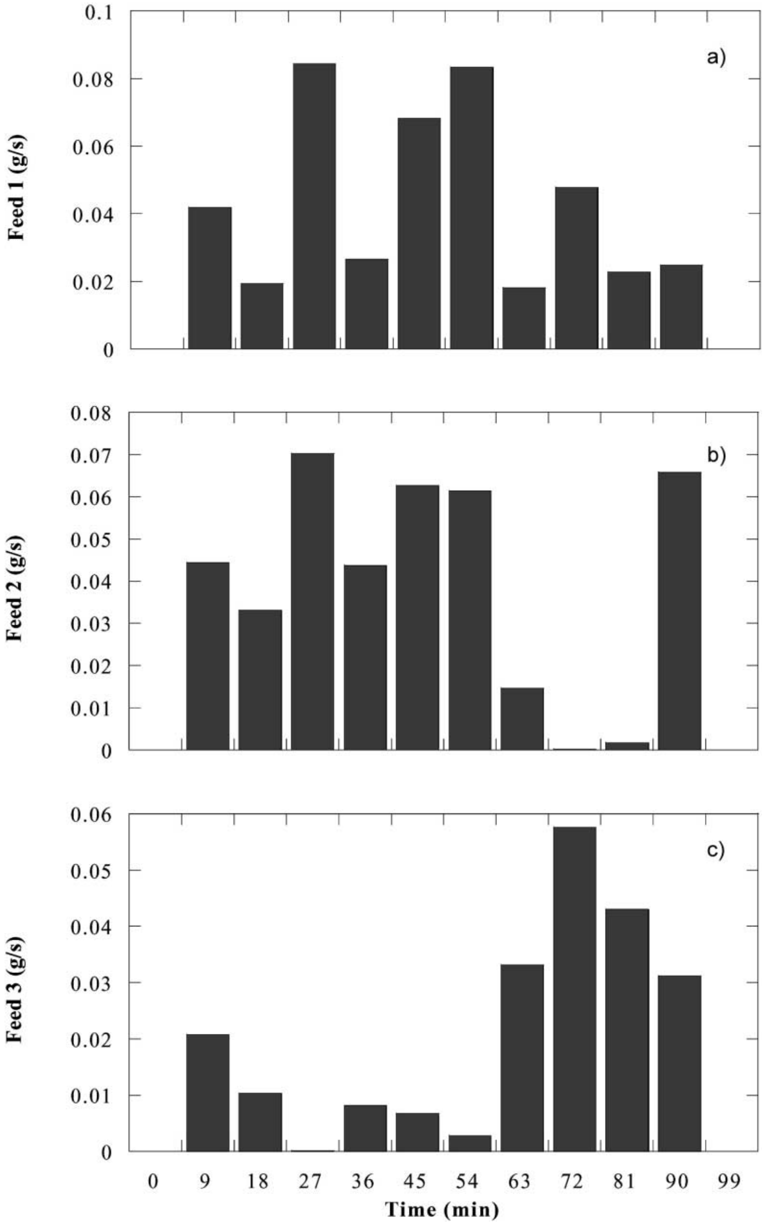

Fig. 1. Flow rate profiles for run C1. (a) Feed 1: *n*-BA, (b) Feed 2: pre-emulsion containing MMA and (c) Feed 3: pre-emulsion containing CTA and MMA.

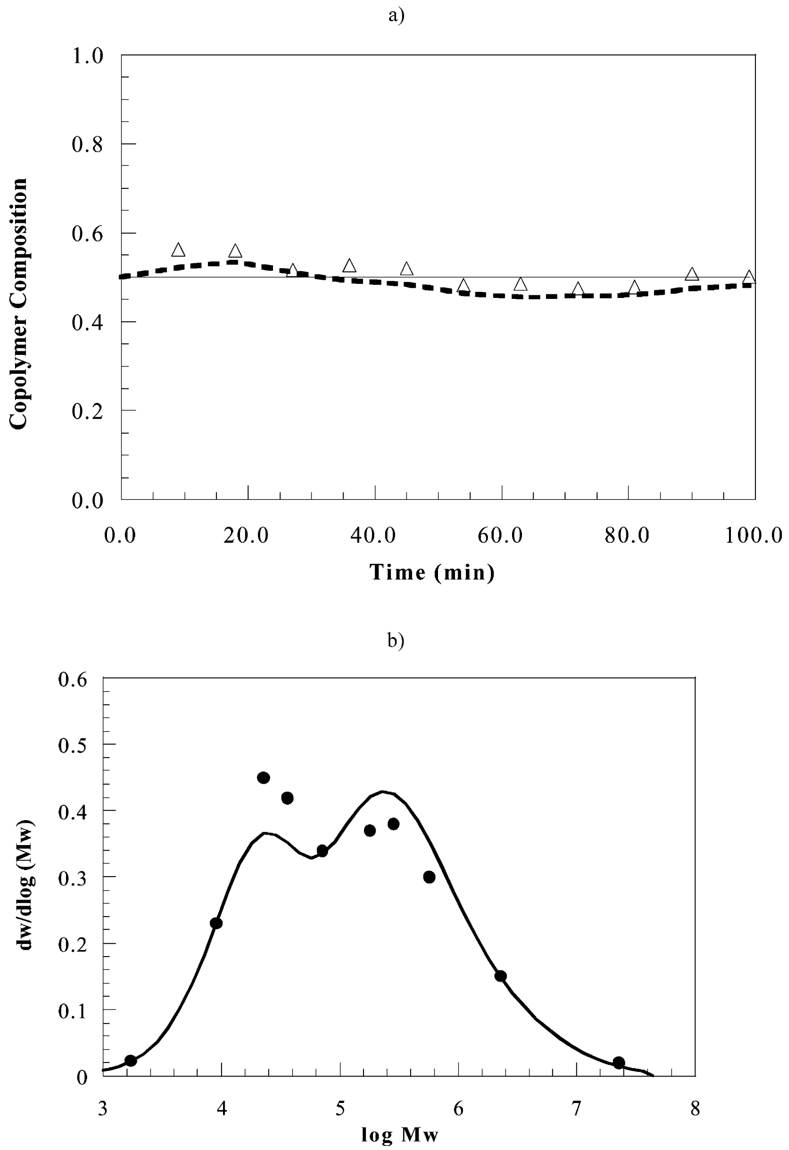

Fig. 2. (a) Evolution of cumulative copolymer composition referred to MMA in run C1. Legend: (—–) desired composition; (- - -) composition obtained in the optimization; (△) experimental composition. (b) Simulated MWD obtained in optimization in Case C1. Legend: (●) desired MWD; (—–) MWD obtained in optimization.

Table 2
Formulation of the seeded emulsion copolymerization, Case C2 (80 °C, 200 rpm, feed time = 70 min)

	Initial charge	Feed 1	Feed 2	Feed 3
MMA (g)	–	–	146.55	36.30
n-BA (g)	–	234.30	–	–
AA (g)	–	2.34	1.47	0.36
CTA: *n*-dodecanethiol (g)	–	–	–	2.98
Water (g)	650.00	–	113.00	28.00
Emulsifier: Alipal CO-436 (g)	0.4	–	1.30	0.30
Initiator: $K_2S_2O_8$ (g)	1.50	–	–	–
Buffer: $NaHCO_3$ (g)	1.50	–	–	–
Seeds[a] (g)	150.0	–	–	–

[a] $N_{\text{pseed}} = 1 \times 10^{17}$ particles.

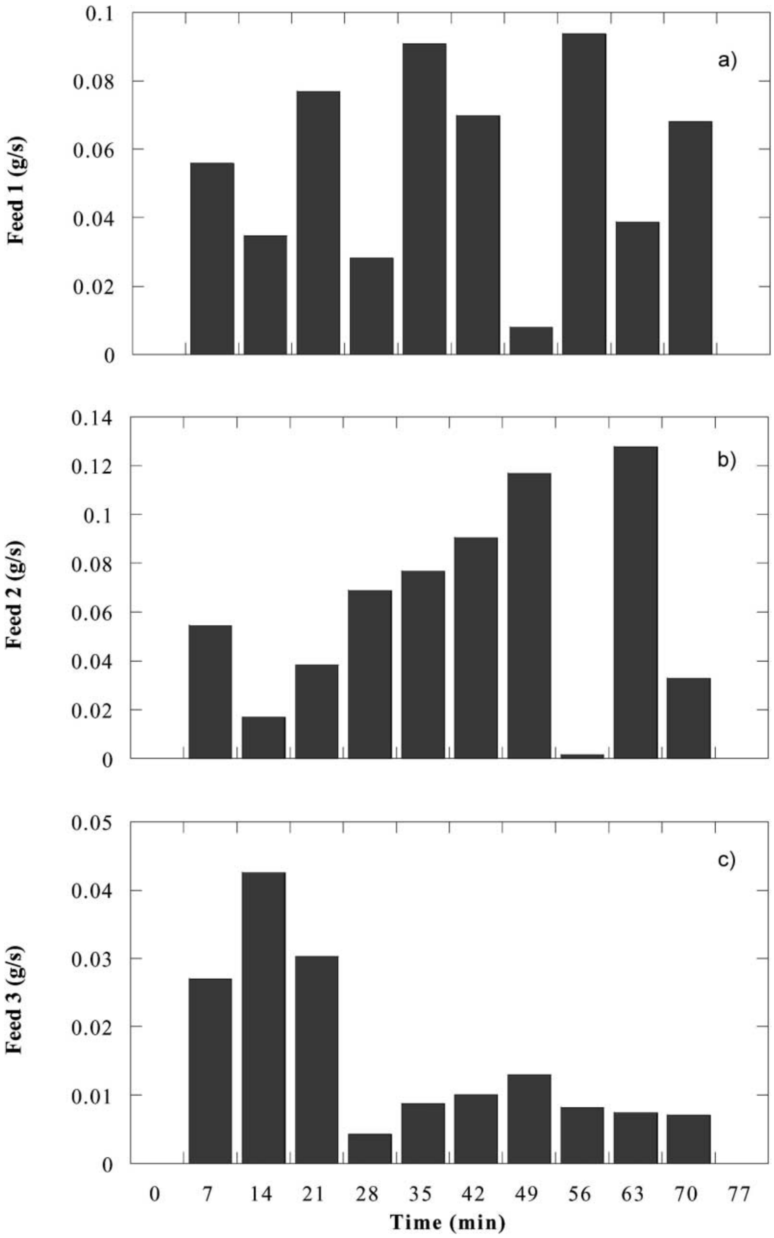

Fig. 3. Flow rate profiles for run C2. (a) Feed 1: *n*-BA; (b) Feed 2: pre-emulsion containing MMA and (c) Feed 3: pre-emulsion containing CTA and MMA.

3. Experimental

3.1. Reagents

Doubly deionized water was used in all polymerizations. Monomers (MMA and *n*-BA from Rhodia) were washed several times with 10 wt.% aqueous sodium hydroxide solutions. Other reactants as CTA (*n*-dodecanethiol, Aldrich), acrylic acid (AA, Rhodia), emulsifier (Alipal CO-436, Rhodia), initiator ($K_2S_2O_8$, Fluka), and buffer ($NaHCO_3$, Panreac) were used as supplied without further purification.

3.2. Experimental procedure

Seeded emulsion polymerizations were used to avoid particle nucleation, which might be difficult to reproduce. Polymer seeds with solids content of 34% were prepared under starved conditions at 80 °C, using a feeding time of 6 h. At the end of the feeding period, the seeds were kept at 90 °C for 16 h to ensure complete decomposition of the initiator. Table 3 presents the formulation used to prepare the seeds.

The experimental implementation of the optimal copolymerizations (Cases C1 and C2) was carried out at 80 °C in a

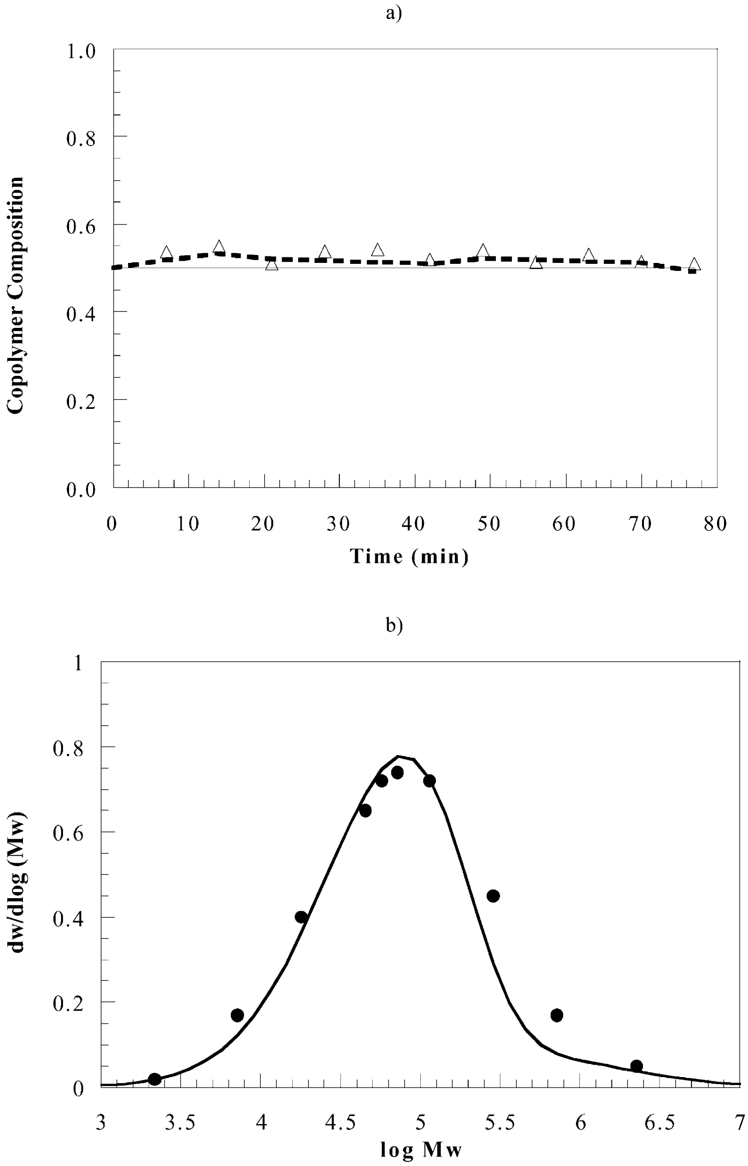

Fig. 4. (a) Evolution of cumulative copolymer composition referred to MMA in run C2. Legend: (——) desired composition; (- - -) composition calculated in the optimization; (△) experimental composition. (b) MWD obtained in optimization in Case C2. Legend: (●) desired MWD; (——) MWD obtained in optimization.

Table 3
Formulation used to prepare the seeds ($T = 80°\mathrm{C}$, 200 rpm)

	Initial charge	Feed 1	Feed 2
MMA (g)	–	223.62	–
n-BA (g)	–	286.00	–
AA (g)	–	5.10	–
Water (g)	236.20	–	734.15
Emulsifier: Alipal CO-436 (g)	2.15	–	11.74
Initiator: $K_2S_2O_8$ (g)	0.1	–	0.88
Buffer: $NaHCO_3$ (g)	0.1	–	0.88

modified reaction calorimeter (RC1, Mettler-Toledo) [27,28] using the formulations given in Tables 1 and 2. The optimal feed flow rates of monomers and CTA given in Figs. 1 and 3 were experimentally implemented. The flow rates were controlled by the equipment by means of a PI controller for every 20 s. In addition, the modified calorimetric reactor allows the heat of reaction and hence the unreacted amounts of monomers and CTA to be estimated as described in Refs. [8,9].

3.3. Latex characterization

Conversion: Conversion (x) was calculated by gravimetry and estimated on-line from calorimetric data.

Composition: Cumulative molar composition of copolymer referred to MMA (y_{MMA}) was calculated from the unreacted amounts of monomer measured by gas chromatography, GC and the material balances of the monomers.

Molecular weight distribution: The MWDs were determined by SEC. The SEC apparatus was equipped with a pump (Waters, model 410) and a dual detector: refractometer and viscometer (Viscotek, model 250). A series of three Styragel columns with pore sizes of 10^2, 10^4 and 10^6 Å (HR2, HR4 and HR6 from Waters) were used. Temperature was kept constant at 40 °C on both detectors and columns. Tetrahydrofuran (THF) was used as solvent at a flow rate of 1.0 ml/min.

4. Results and discussion

The polymer considered in this work, MMA/*n*-BA, is a non-linear copolymer; namely transfer to polymer occurs in a significant extent during the polymerization leading to the formation of branched and, in some cases, gelified polymer. It has been shown [17] that the closed-loop strategies developed for linear polymers [9] may fail because the inactive polymer formed in the process may become active (due to transfer to polymer reactions) modifying its molecular weight. Therefore, an open-loop control strategy was implemented.

4.1. Case C1

Fig. 5 presents the evolution of the simulated optimal overall conversion and that obtained gravimetrically during the experiment. Fig. 2b shows the copolymer composition as calculated by GC when the feed rates of Fig. 1 were implemented. It can be seen a good concordance between the desired copolymer composition and that obtained experimentally.

Fig. 6 compares the conversion evolution of the MWD obtained during the experiment and that calculated in the optimization. Agreement may be regarded as excellent for an open-loop control policy. One must observe that the final MWD is bimodal, as desired and predicted by the model. It can be seen that a high molecular weight polymer was initially produced, whereas the low molecular weight was mainly formed at the end of the process. The MWD produced was slightly narrower than the predicted in the optimization. This could be due to diffusional limitations of CTA to reach the polymer particles. This effect can be clearly seen at 82% of conversion where the MWD predicted by the model shows a low molecular weight shoulder, but the MWDs produced in the experiment are still unimodal or the shoulder is at larger molecular weights, indicating that the CTA required some additional time to reach the polymerization loci. Note that the model employed in the optimization did not account for mass transfer of CTA because in seeded semibatch experiments feeding CTA at a constant flow rate and pre-emulisified there was not evidence of mass transfer limitations [22]. In addition, model predictions using a literature value for the chain-transfer rate constant ($C_{\mathrm{CTA}} = 0.711$) [29] allowed to fit experimental data of MWD reasonably well. However, the requirements of the optimal policy are more exigent because a sudden increase of the CTA concentration in the polymer particles is required to produce the low molecular weight mode. Results in Fig. 6 show that improvements can be achieved by using a model that accounts for the diffusional limitations [30]. It is worth mentioning that such a model involves parameters that depend on the flow patterns in the reactor which reduce the prediction capability of the model.

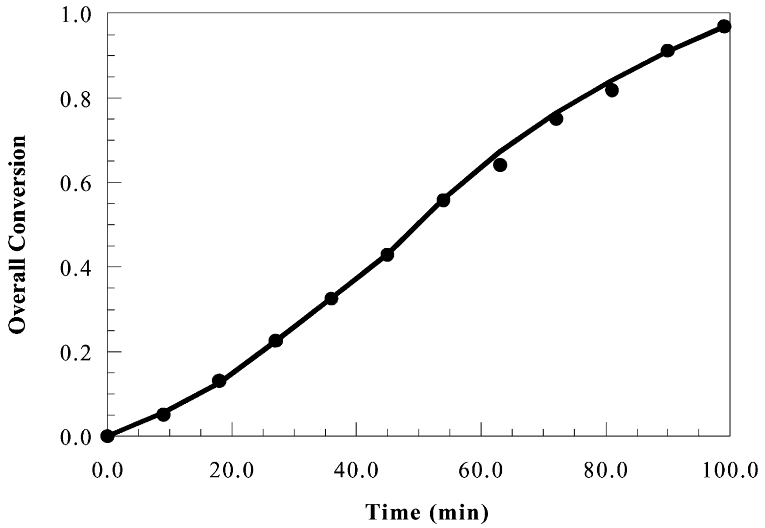

Fig. 5. Evolution of conversion during run C1. Legend: (——) mathematical model; (●) gravimetric conversion.

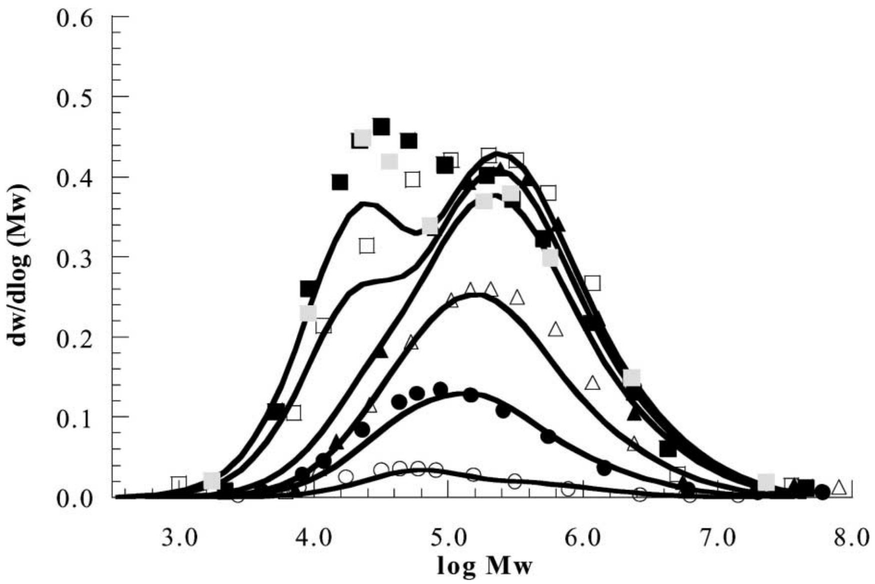

Fig. 6. Comparison between the evolution of the desired final MWD (▨), the MWD obtained in the optimization (—–) and the MWD obtained during run C1. (○) $x = 5\%$, (●) 22%, (△) 43%, (▲) 64%, (□) 82%, (■) 97%.

Circumstantially, it turned out that the final MWD of the copolymer produced in the experiment was closer to the originally desired (gray squares) MWD.

4.2. Case C2

The second case considered was the production of a copolymer with a unimodal MWD (Fig. 4b) and a 50/50 molar copolymer composition.

Fig. 7 presents both the evolution of overall conversion calculated experimentally and simulated by the model. Fig. 4a presents the copolymer composition determined by means of GC (open triangles) during the reaction when the feed rates of Fig. 3 were implemented. A good agreement between desired and experimental values for conversion and desired composition can be observed.

Fig. 8 shows the conversion evolution of the MWD obtained in the experiment. This figure shows that the desired MWD was reproduced almost perfectly using the monomer and CTA feed profiles calculated through the optimization approach (Fig. 3). There is a slight deviation to lower molecular weights in the final distribution that apparently started deviating at 60%. This may be due to the fact that most of the CTA is fed at the beginning of the process (see Fig. 3c) and hence if the CTA is slightly diffusionally limited, it can accumulate at the beginning of the process yielding lower

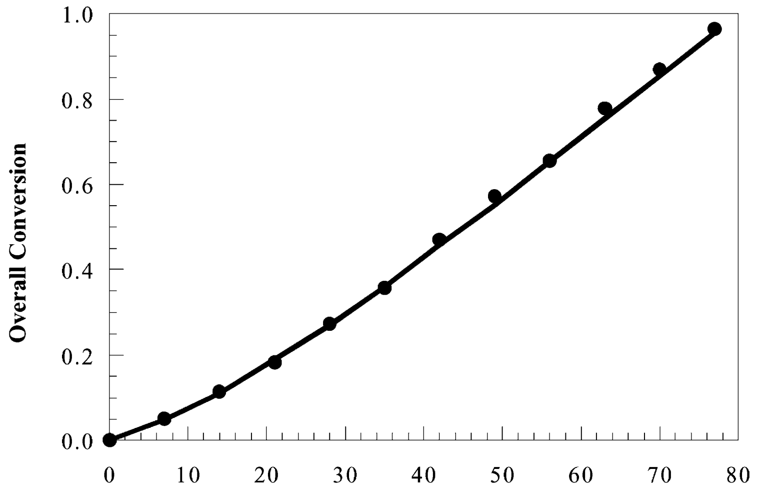

Fig. 7. Evolution of conversion during run C2. Legend: (—–) mathematical model; (●) gravimetric conversion.

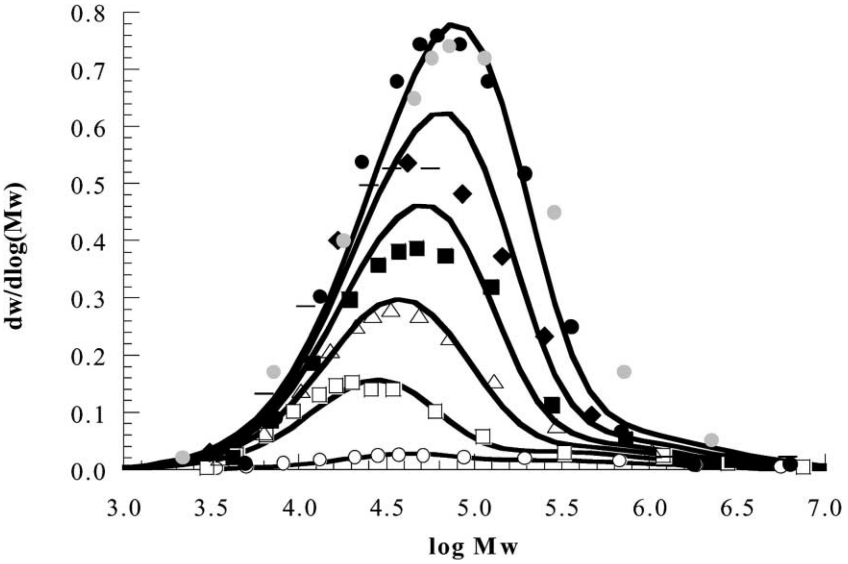

Fig. 8. Comparison between the evolution of the desired final MWD (●), the MWD obtained in the optimization (——) and the MWD obtained during run C2. (○) $x = 5\%$, (□) 18%, (△) 36%, (■) 57%, (◆) 78%, (●) 96%.

molecular weights than those required at the end of the process.

As far as we know this is the first time that the simultaneous control of copolymer composition and the entire MWD (not only average values) of non-linear (branched) emulsion copolymers is achieved in real-time experiments by means of an open-loop control strategy.

5. Conclusions

This work focused on the open-loop control of non-linear emulsion copolymers with desired copolymer composition and MWD. IDP was used to compute optimal monomer and CTA feed profiles using a detailed mathematical model for emulsion copolymerization. The production of copolymers of MMA/*n*-BA was considered: the first case was a copolymer with 50/50 molar composition and bimodal MWD, whereas the second case was also a copolymer with 50/50 molar composition, but with a broad and unimodal MWD. The real-time implementation of the optimal trajectories for monomer and CTA for the two cases was successfully carried out and the copolymers produced were certainly close to those desired. Note that the success of the open-loop strategy is basically due to the goodness of the mathematical model and the lack of non-modeled disturbances during the real-time experiments. Nevertheless, work is being conducted in our labs to develop robust closed-loop control strategies to deal with the simultaneous control of copolymer composition and MWD of non-linear emulsion copolymers and this will be the topic of future papers.

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