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Emulsion polymerization of styrene. Use of *n*-nonyl mercaptan for molecular weight control

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Abstract

The unseeded emulsion polymerization of styrene with *n*-nonyl mercaptan (*n*NM) as chain transfer agent (CTA) was investigated, with the aim of producing a PS latex of a low molecular weight polydispersity at high conversion and in short reaction times. To this effect, starved and minimum time semibatch reactions were investigated and compared to equivalent batch polymerizations. The high reactivity of *n*NM with respect to the monomer makes it feasible to implement a minimum time policy with intermediate addition of CTA only. The MWDs of the minimum time runs were intermediate between the broader distributions of the batch reactions and the narrower distributions of the starved experiments. The conversion profiles of minimum time experiments almost coincided with those of equivalent batch polymerizations. For controlling MWDs through semibatch operations, it seems preferable to use *n*NM instead of other (less reactive and more common) CTAs like *tert*-dodecyl mercaptan or CCl_4. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Styrene emulsion polymerization; Nonyl mercaptan; Molecular weight control

1. Introduction

Chain transfer agents (CTAs) or 'modifiers' are normally included in emulsion polymerization recipes to lower the molecular weights of the obtained polymers [1]. In industrial practice, *tert*-dodecyl mercaptan (*t*DM) and CCl_4 are possibly the most common CTAs; but the use of CCl_4 is presently being reduced for environmental reasons.

Some important CTA properties are their water solubility, their mass transfer resistance to diffusion between phases, and their 'effective' reactivity ratio $C_X = k_{fX}/k_p$ (where k_{fX} is the chain transfer constant to the CTA, k_p is the propagation rate constant and C_X is an effective rather than a true reactivity ratio because the chain transfer reaction may be diffusion controlled.) The mentioned properties are interrelated, and affect not only the molecular weights but also (indirectly) the polymerization rate [1–6].

Nonyl mercaptans such as *tert*-nonyl mercaptan (*t*NM) and *n*-nonyl mercaptan (*n*NM) have been relatively little applied and investigated. The use of *t*NM was investigated in a patent for producing a styrene–butadiene rubber (SBR) [7], and in the batch and semibatch emulsion polymerization of styrene (St) [5,6]. The effects of *n*NM on the emulsion polymerization of chloroprene were analyzed by Barsegyan and Bagdasaryan [8] and Karapetyan et al. [9]. For the polymerization of St with *n*NM and other CTAs, Nomura et al. [4] modelled the CTA mass transport from the monomer droplets into the polymer particles.

For batch emulsion polymerizations, Echevarría et al. [10], Salazar et al. [5], Harelle et al. [6], Uraneck and Burleigh [11], and Weerts et al. [12] investigated the effects of CCl_4 and various commercial mercaptans on the molecular weights of polystyrene (PS), polybutadiene, and SBR. Suddaby et al. [13] and Bon et al. [14] have, respectively, applied a 'catalytic CTA' and the so-called 'controlled radical polymerization technique', for producing materials of low molecular weights and polydispersities in batch reactors. On the other end of the continuous emulsion polymerizations, Gugliotta et al. [15] and Vega et al. [16,17] have theoretically investigated the manipulation of *t*DM for controlling the molecular weights of SBR.

Were it not for the long times involved, the uniform and starved addition of monomer and CTA would be otherwise ideal for producing a constant and narrow MWD. (In a truly starved operation, the instantaneous fractional conversion of the added reagents is close to 100%, and the volume of the monomer–CTA droplets phase is close to zero.) Paine et al. [18] patented a starved technique for controlling the MWD of a St–butyl acrylate copolymer by slow addition of a

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preemulsified CTA–comonomer mixture. Harelle et al. [6] carried out a preseeded and semistarved polymerization of St for controlling the molecular weights of PS, but relatively broad MWDs were obtained. For the polymerization of St with *t*NM or *t*DM, Salazar et al. [5] produced almost Schulz–Flory or 'most probable' MWDs in reaction times that were five times greater than equivalent batch times.

Applying intermediate mercaptan injections, Uraneck and Burleigh [19] narrowed the MWD of a SBR with respect to the batch. Baus and Swift [20] investigated the intermediate addition of CTA for broadening the MWD of polyacrylic contact adhesives. More recently, PS latexes with prespecified variations of the molecular weights were synthesized through a closed-loop strategy that involved the intermediate addition of monomer and CTA together with the on-line measurement of their global concentrations [10].

The monomer and/or CTA feed profiles required in a MWD control can be determined through open- or closed-loop control strategies. Open-loop methods do not normally require on-line polymer quality measurements, and are based on somehow inverting a process model [16,17,19]. Closed-loop policies are based on measuring (or estimating) the controlled variable; that in our case can be represented by an average molecular weight [10]. The on-line molecular weight measurement is expensive, the equipment is difficult to maintain, and the results are delayed by the sample preparation and fractionation. But while open-loop results are totally dependent on the model accuracy, closed-loop operations may not even require a process model. Many industrial emulsion polymerizations consist of a series of semibatch operations. In this case, the following intermediate approach between the open- and the closed-loop is possible: each semibatch operation is carried out in open-loop, but the feed policy for the following run is calculated on the basis of off-line polymer quality measurements from the previous run. In emulsion processes, this idea has been applied to control copolymer composition [21], but no applications on the molecular weight control have been found.

In this work, the emulsion polymerization of St with *n*NM is investigated with the aim of producing narrow MWDs of prespecified final $\bar{M}_n$ values at high conversion and in the shortest possible times. To this effect, two open loop and semibatch operations were investigated and compared to equivalent batch reactions. For calculating the CTA feed profiles of the minimum time experiments, an existing polymerization model was used [5]. As far as the authors are aware, this work is the first report on the application of *n*NM for controlling the MWD of a latex.

2. Theoretical considerations

In an ideal molecular weight control via CTA addition, most of the accumulated polymer is produced by transfer reactions to the CTA, and the global CTA concentration negligibly affects the polymerization rate [1]. Under such conditions, the instantaneously produced polymer exhibits a most probable or Schulz–Flory MWD with a polydispersity $\bar{M}_{\mathrm{w,inst}}(t)/\bar{M}_{\mathrm{n,inst}}(t) \cong 2$ and a number-average molecular weight given by [5]:

$$\bar{M}_{\mathrm{n,inst}}(t) = \frac{M_{\mathrm{S}}}{C_{\mathrm{X}}} \frac{[S]_{\mathrm{p}}(t)}{[X]_{\mathrm{p}}(t)} \quad (1)$$

where M_{S} is the monomer molecular weight; $[S]_{\mathrm{p}}$, $[X]_{\mathrm{p}}$ are the molar concentrations of monomer and CTA in the polymer particles; and C_{X} is normally adjusted to batch experiments [22].

If a batch polymerization with $C_{\mathrm{X}} = 1$ is carried out, then the concentration ratio $[S]_{\mathrm{p}}(t)/[X]_{\mathrm{p}}(t)$ remains constant along the reaction, and therefore $\bar{M}_{\mathrm{n,inst}}(t)$ is also constant (Eq. (1)). For reactive CTAs exhibiting $C_{\mathrm{X}} > 1$, then $\bar{M}_{\mathrm{n,inst}}(t)$ increases in the course of the batch reaction; while it decreases for CTAs with $C_{\mathrm{X}} < 1$.

For any arbitrary C_{X} value, a constant $\bar{M}_{\mathrm{n,inst}}(t)$ may be still obtained if the reaction is carried out under a starved addition of the monomer-CTA mixture. In this case, the shortest total polymerization time that produces a constant $\bar{M}_{\mathrm{n,inst}}(t)$ is determined by: (a) the monomer consumption when $C_{\mathrm{X}} > 1$; and (b) the CTA consumption when $C_{\mathrm{X}} < 1$. Thus, a system with $C_{\mathrm{X}} > 1$ seems preferable for shortening the starved operation.

Consider a starved polymerization with addition of a monomer–CTA mixture. If the instantaneous fractional conversions of monomer and CTA are close to 100%, then it is relatively straightforward to calculate the monomer–CTA molar feed ratio for producing any desired number-average molecular weight $\bar{M}_{\mathrm{n}}^{\mathrm{d}}$. In effect, from the monomer and CTA molar balances under steady state conditions, one obtains [5]:

$$\frac{F_{\mathrm{S,in}}}{F_{\mathrm{X,in}}} \cong \frac{\bar{M}_{\mathrm{n}}^{\mathrm{d}}}{M_{\mathrm{S}}} \quad (2)$$

where $F_{\mathrm{S,in}}$ and $F_{\mathrm{X,in}}$ are, respectively, the monomer and CTA molar feed rates.

In a practical starved operation, a compromise between the MWD breadth and the total reaction time may be required. In this work, we shall call 'starved', any polymerization where all the monomer and CTA are added along the entire reaction time at a uniform feed rate. When such a process is excessively shortened, then: (i) the MWD is broadened; (ii) the final monomer and CTA conversions may be lower than required; and (iii) the CTA and/or the monomer concentrations in the polymer particles may be below equilibrium conditions [5], and therefore Eq. (2) is no longer applicable. In Appendix A, a simple model for calculating the CTA concentration in the polymer particles under a restricted CTA diffusion is presented. Unfortunately, such a model is of a limited use, due to the difficulty in estimating the CTA diffusion parameters.

For systems with $C_{\mathrm{X}} > 1$, it is possible to develop a

Table 1
Recipes and main global results

Experiments	Batch			Starved			Minimum time	
	B1	B2	B3	S1	S2	S3	M1	M2
Initiator: $K_2S_2O_8$ (g)	0.2367	0.2320	0.2322	0.4071	0.4022	0.4121	0.2338	0.2275
Emulsifier: SLS (g)	2.610	2.604	2.603	3.903	3.901	3.935	2.6061	2.6038
Buffer: $NaCO_3H$ (g)	0.1950	0.2330	0.2367	0.2002	0.2362	0.2142	0.2330	0.2307
DDI water (g)	516.2	515.7	516.0	515.6	516.4	516.3	515.2	516.8
Styrene total load (g)	129.31	130.01	129.38	137.0	129.9	140.9	130.00	129.90
*n*NM total load (g)	1.315	0.8480	1.560	1.382	1.313	1.422	1.339	0.6837
*n*NM to St global ratio (pphm)	1.0	0.65	1.2	1.0	1.0	1.0	1.0	0.5
Styrene initial load (g)	129.31	130.01	129.38	–	–	–	127.00	125.92
*n*NM initial load (g)	1.315	0.8480	1.560	–	–	–	0.6217	0.3100
Total St–*n*NM feed (g)	–	–	–	138.4[a]	131.2[a]	142.3[a]	3.717[b]	4.354[c]
Constant St–*n*NM feed (g/min)	–	–	–	0.3373	0.6695	1.5136	–	–
Total reaction time (min)	130.0	155.0	150.0	408.0	196.0	94.0	150.0	150.0
$\bar{M}_n^d$ (g/mol)	–	–	–	16,000	16,000	16,000	16,000	30,000
Final monomer conversion (%)	97.3	98.1	98.6	90.6	91.0	80.5	99.9	97.3
Reaction time for $x = 95\%$ (min)	80.0	80.0	75.0	–	–	–	60.0	85.0
$\bar{M}_n$ (g/mol)	18,700	24,700	13,400	17,500	16,300	17,700	16,600	33,100
$\bar{M}_w$ (g/mol)	66,800	1,16,200	52,500	35,900	32,200	35,800	40,200	77,000
$\bar{M}_w/\bar{M}_n$	3.57	4.70	3.92	2.05	1.98	2.02	2.42	2.33

[a] Constantly delivered along the total reaction time.
[b] Added in 13 impulsive injections.
[c] Added in 12 impulsive injections.

semibatch molecular weight control strategy involving only the intermediate addition of CTA. In Appendix B, a method for calculating the CTA feed profile that ideally yields a fixed Schulz–Flory MWD is presented. Since all the monomer and initiator are added at the reaction start, such operation can be also regarded as 'minimum time' from the point of view of the monomer conversion.

For systems with $C_X < 1$, the MWD control may require only the intermediate addition of monomer, or the independent and simultaneous addition of monomer and CTA. Compared to the case of $C_X > 1$, the total polymerization time is increased and the practical implementation becomes more complicated. Finally, note that even for systems with $C_X > 1$, it may be still necessary to include an independent monomer feed. This may occur when for example the reactor cooling capacity is low, and therefore the polymerization rate must be maintained below certain limits.

3. Experimental work

Polymerizations were carried out in a 0.8 dm^3 glass reactor equipped with a modified anchor stirrer, a sampling system, and an N_2 inlet. The temperature was controlled at 70°C by means of a thermostatic bath, and it was monitored with a digital thermometer. The stirring rate was 200 rpm.

Distilled and deionized (DDI) water was used throughout the work. The following reagents were used as received: the emulsifier sodium lauryl sulphate (Mallinckrodt, 95% purity); the initiator $K_2S_2O_8$ (Mallinckrodt, 99% purity); the buffer salt $NaCO_3H$ (Anedra, 99.7% purity); and the CTA *n*NM (Fluka Chemika, >95% purity). The monomer was prepared as follows: commercial grade St (PASA SA, Argentina) was first washed several times with a 15% KOH solution, then washed with DDI water until neutral wash waters, and finally dried with $CaCl_2$.

The following experiments were carried out: three batch (B1–B3), three starved (S1–S3), and two minimum time (M1,M2). The recipes are presented in the upper part of Table 1.

In the starved (or better, semistarved) experiments, the St–*n*NM mixture was fed at a constant rate by means of a syringe pump. In the minimum time runs, a sufficiently small variable speed pump was not available. For this reason, the continuous CTA feed was replaced by a train of manual injections introduced through a 1 cm^3 syringe. To increase the volume of such injections, a *n*NM–St mixture (rather than pure CTA) was used. The amount of monomer introduced through the manual injections was small with respect to the initial monomer load (Table 1).

Samples were withdrawn along the reactions, and the following was measured: (i) the total monomer conversion x, by gravimetry; (ii) the unswollen average particle diameter $d_{p,unsw.}$, with a Brookhaven BI-9000 AT dynamic light scattering photometer; and (iii) the MWDs and their averages, with a Waters ALC220 size exclusion chromatograph. In the semibatch reactions, the fractional monomer conversion (i.e. based on the monomer added up to each sampling time) was also gravimetrically determined.

To simulate the experiments and to calculate the

Table 2
*n*NM model parameters at 70°C

Parameter	Value	Reference
$D_{wX}\delta$	0.40×10^{-7} dm²/min	Salazar et al. [5]
C_X	1.9	Adjusted in this work[a]
K_{Xdw}	7.00×10^{5}	Nomura et al. [4]
K_{Xwp}	2.22×10^{-6}	Nomura et al. [4]
$k_{X,wt}A_d$	2.5×10^{3} dm³/min	Adjusted in this work[b]

[a] To the batch measurements.

[b] To the minimum time measurements.

minimum time feeds, the mathematical model of Salazar et al. [5] was applied. Except for the model parameters associated to *n*NM (Table 2), all other parameters were directly taken from our previous publication [5]. The diffusion coefficient of *n*NM radicals in the polymer phase is represented by the product $D_{wX}\delta$, and its value was adopted identical to that of *t*NM [5]. The C_X ratio was adjusted to fit the $\bar{M}_n$ measurements of the batch experiments. The partition coefficients K_{Xdw} and K_{Xwp} were taken from Nomura et al. [4]. In the simulations of the batch experiments, the CTA was assumed in equilibrium between the phases. In the semibatch simulations, an increased mass transfer resistance for the CTA flow with respect to the batch case could be implemented. The diffusion resistance is represented by the inverse of $k_{X,wt}A_d$ (Appendix A). This factor was adjusted to the $\bar{M}_n$ and $\bar{M}_w$ measurements of the minimum time runs (Table 2). This increased diffusion resistance was seen unnecessary for simulating the starved experiments.

A global *n*NM to St mass ratio of 1 pphm (parts per hundred monomer) was used in experiments B1, S1–S3, and M1 (Table 1). In Fig. 1, the final MWDs of experiments B1, S2, and M1 are compared with a Schulz–Flory MWD of $\bar{M}_n^d = 16,000$ g/mol. Figs. 2–5 present the measurements and model predictions of the batch, starved, and minimum time experiments. The lower rows of Table 1 contain the final monomer conversions, the reaction times for a 95% monomer conversion, the average molecular weights, and the polydispersities.

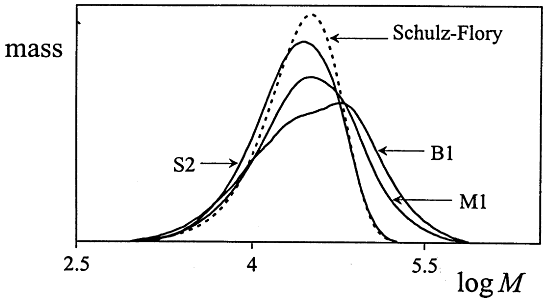

Fig. 1. Final MWDs of the batch experiment, B1; the starved experiment, S2; and the minimum time experiment, M1. The desired theoretical Schulz–Flory MWD with $\bar{M}_n^d = 16,000$ g/mol is also represented.

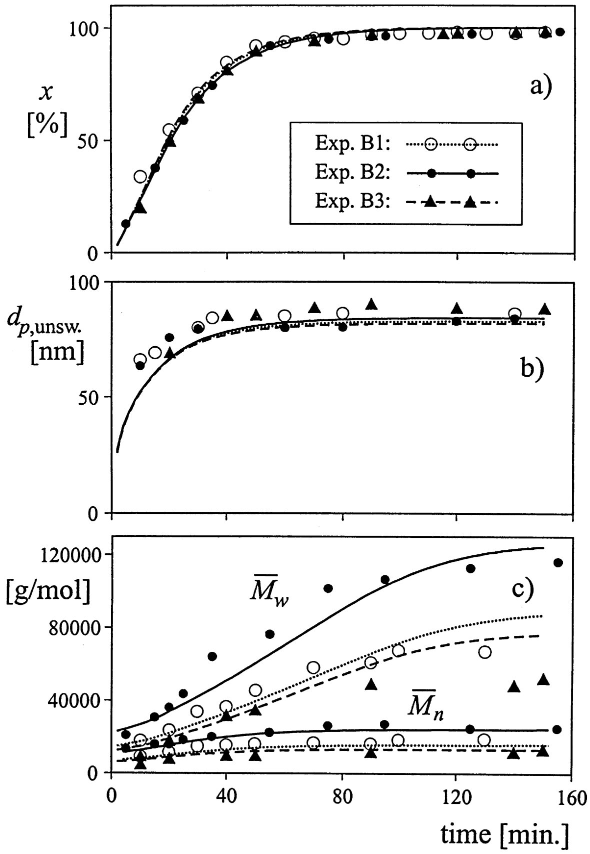

Fig. 2. The batch experiments. (a) Evolution of the total conversion. (b) The unswollen average particle diameter. (c) The average molecular weights.

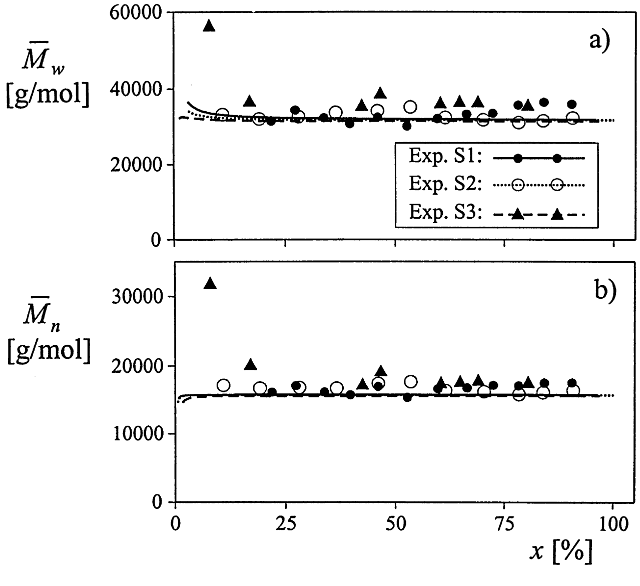

Fig. 3. The starved experiments. Evolution of the average molecular weights.

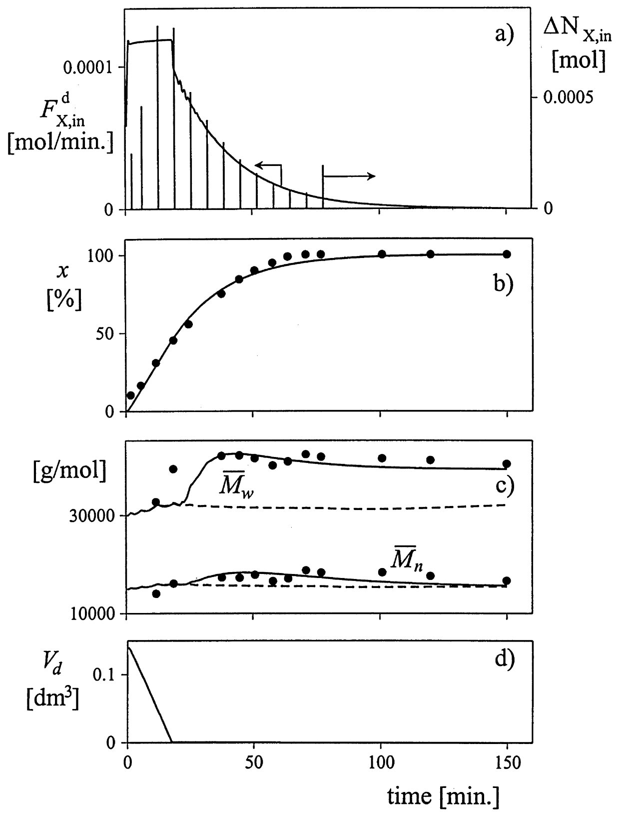

Fig. 4. Minimum time experiment, M1. (a) Continuous CTA feed profile and applied discrete profile. (b) Monomer conversion. (c) Average molecular weights (discontinuous trace: model predictions assuming a CTA partition according to equilibrium; continuous trace: predictions assuming a restricted CTA diffusion). (d) Predicted evolution of the monomer–CTA droplets phase.

3.1. Batch experiments

The emulsifier and buffer salt were dissolved in ~500 g of DDI water and were loaded into the reactor. Then, the St and the *n*NM were charged; the mixture was stirred for about 30 min; and the temperature was stabilized at 70°C. To start the polymerization, the initiator was dissolved in the remaining water and the solution was loaded into the reactor.

From Figs. 1 and 2 and Table 1, the following can be noted: (i) the CTA concentration negligibly affects the monomer conversion and particle diameters; (ii) the increasing average molecular weights indicate a reactive CTA; and (iii) the relatively high final $\bar{M}_n$ values and polydispersities may be explained by a total CTA consumption at high monomer conversions. (According to the model, the global CTA concentration is half its original value at a monomer conversion of around 30%.) The adjusted C_X (1.9) is close to previously reported values for *t*NM [5,6].

3.2. Starved experiments

Starved reactions were carried out with the aim of obtaining a narrow MWD with $\bar{M}_n^d = 16,000$ g/mol in moderate reaction times. The emulsifier–buffer solution was charged into the reactor, the temperature was stabilized, the initiator solution was added, and the St–*n*NM mixture was fed at a constant rate.

In experiment S1, the reaction time was selected about five times longer than the batch times for a monomer conversion of 95%. In experiments S2 and S3, shorter periods were adopted. The final monomer conversions are all below the batch values. In experiment S1, the fractional monomer conversion varied from 80% at the beginning of the run to 92% at the reaction end. In the shorter experiment S3, the initial fractional conversion was as low as 60%. Thus, truly starved conditions were not reached. However, the final polydispersities are all close to the ideal value of two (Table 1). The average molecular weights are almost constant in S1 and S2, while a drop in the molecular weight profiles is observed at the beginning of S3 (Fig. 3).

3.3. Minimum time experiments

The desired $\bar{M}_n$ values of experiments M1 and M2 were 16,000 and 30,000 g/mol, respectively. The initial loads and continuous CTA feed profiles were calculated through Eqs. (B10) and (B4), respectively. Since the mass resistance parameter was a priori unknown, the CTA profile was calculated assuming that such a reagent was partitioned according to thermodynamic equilibrium. The required control strategy is presented in Table 1 and in Figs. 4(a) and 5(a). The feed profiles are approximately constant until disappearance of the monomer–CTA droplets, and thereafter decreasing (see theoretical predictions of Figs. 4(d) and 5(d)). According to the mathematical model, the conversion profiles are close to the batch conversion profiles.

Experiments were carried out as follows. The initial charge consisted of the emulsifier–buffer solution, most of the monomer, and the necessary amount of CTA. After temperature stabilization, the initiator was loaded to start the runs and the remaining *n*NM was incorporated in the way of 12 or 13 discrete additions (Table 1 and Figs. 4(a) and 5(a)).

The evolution of the monomer conversion and average molecular weights is shown in Figs. 4(b),(c) and 5(b),(c). As expected, the conversion profiles are similar to the batch, and the final $\bar{M}_n$ values are close to the desired values. However, a rapid increase in $\bar{M}_w$ is observed after disappearance of the monomer droplets phase (Figs. 4(d) and 5(d)); thus explaining the relatively high final polydispersities. The total conversion is little affected by the global CTA concentration; and accordingly the conversion predictions are unaffected by the CTA concentration in the polymer particles. In contrast, the average molecular weights are underestimated when assuming equilibrium for the CTA (dashed traces in Figs. 4(c) and 5(c)). Such predictions (and especially the $\bar{M}_w$ estimates) can be considerably improved (continuous traces in Figs. 4(c) and 5(c)), after an a posteriori adjustment of the mass transfer product

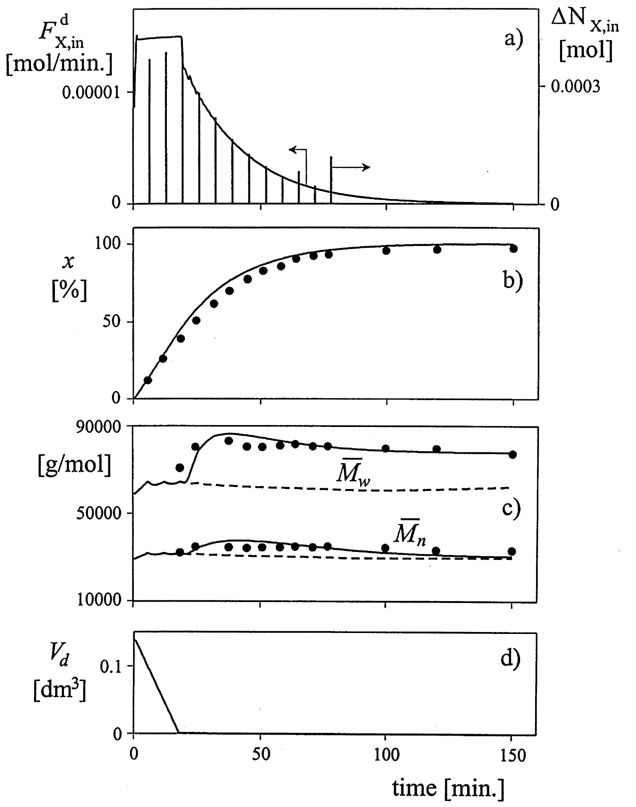

Fig. 5. Minimum time experiment, M2. (a) Continuous CTA feed profile and applied discrete profile. (b) Monomer conversion. (c) Average molecular weights (discontinuous trace: model predictions assuming a CTA partition according to equilibrium; continuous trace: predictions assuming a restricted CTA diffusion). (d) Predicted evolution of the monomer–CTA droplets phase.

$k_{X,wt}A_d$ (Table 2). The model parameter was adjusted on the basis of the measurements of Figs. 4(c) and 5(c).

3.4. Comparison of nNM with other more common CTAs

It seems interesting to compare the *n*NM performance with other more common CTAs such as *t*DM and CCl_4. While for *n*NM it is $C_X > 1$, the same parameter is in the range 0.31–0.51 for *t*DM [5,6] and is equal to 0.098 for CCl_4 [10]. Thus, the following can be immediately noted: (a) in batch polymerizations, the $\bar{M}_n$ and $\bar{M}_w$ profiles are increasing for *n*NM, but decreasing for *t*DM and CCl_4; (b) in starved reactions with constant monomer–CTA addition, the shortest reaction times that yield the desired MWD at a given conversion are always obtained with *n*NM; and (c) the investigated minimum time operations (with addition of CTA only) are not possible with *t*DM or CCl_4.

The *n*NM and *t*DM mercaptans are less water soluble than CCl_4. Thus, while mercaptan radicals are little desorbed from the polymer particles, CCl_4 radicals are moderately desorbed. For this reason, CCl_4 appreciably lowers the conversion profile [10], while *n*NM or *t*DM negligibly affect the polymerization rate [5,6]. The water solubility difference also determines that while the thermodynamic equilibrium assumption is acceptable for the (smaller) CCl_4 molecule, such simplification is more questionable in the case of *n*NM or *t*DM.

4. Conclusions

The emulsion polymerization of St with *n*NM was investigated with the aim of controlling the MWD of the produced PS latex. The increasing average molecular weights of the batch polymerizations indicate a reactive CTA; and the total CTA consumption at high monomer conversions explains the relatively high final $\bar{M}_w$ values and polydispersities. In the starved reactions with constant addition of St–*n*NM, the MWDs were almost Schulz–Flory and with the desired final $\bar{M}_n$ values. However, the final starved conversions were rather low, in spite of the long reaction times of the starved experiments.

The minimum time policy with addition of *n*NM only produced the correct $\bar{M}_n$ values, intermediate polydispersities with respect to equivalent batch and starved experiments, and a conversion profile that was close to the batch. The not so narrow MWDs of the minimum time runs may be explained by the fact that an open-loop strategy was implemented; and the system model did not take into account a controlled CTA diffusion flow. Even though not tested, improved results could be obtained by recalculating the CTA profile considering a controlled CTA diffusion, while simultaneously aiming at a more constant evolution of the average molecular weights. The method could be further improved by implementing a closed-loop strategy with on-line measurement of conversion and/or of the average molecular weights.

For controlling the MWD of a PS latex through semibatch operations, it seems preferable to use *n*NM rather than other more common CTAs like *t*DM or CCl_4.

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Appendix A. Calculation of the monomer and CTA concentrations in the polymer particles

To estimate the monomer and CTA concentrations in the reaction site, the polymerization model of Salazar et al. [5] was applied. The main model assumptions are [5]: (a) the MWD is mainly determined by the chain transfer reactions to the CTA, and it is unaffected by the termination reactions; (b) the monomer is distributed between the phases according to thermodynamic equilibrium, with constant partition coefficients; (c) in the batch runs, the CTA is also partitioned according to equilibrium, while in the semibatch runs the CTA concentration in the polymer particles may be below equilibrium.

From assumption (b), the monomer concentration in the polymer phase is given by [5]:

$$[S]_\mathrm{p} = [S]_\mathrm{p}^\mathrm{e} = \frac{N_\mathrm{S}}{K_\mathrm{Sdw}K_\mathrm{Swp}V_\mathrm{d} + K_\mathrm{Swp}V_\mathrm{w} + V_\mathrm{p}} \tag{A1}$$

where $[S]_\mathrm{p}^\mathrm{e}$ is the monomer concentration in the polymer phase under equilibrium conditions; N_S is the total monomer moles; V_d, V_w, and V_p are the volumes of the (monomer–CTA) droplets phase, aqueous phase, and polymer phase, respectively; and K_Sdw, K_Swp are the St partition coefficients between droplets–aqueous phases, and between aqueous–polymer phases, respectively.

As in Salazar et al. [5], the following expression is used for calculating the CTA concentration in the polymer particles (when such variable is suspect of being below thermodynamic equilibrium):

$$[X]_\mathrm{p} = \frac{\dfrac{N_\mathrm{X}}{K_\mathrm{Xdw}K_\mathrm{Xwp}V_\mathrm{d} + K_\mathrm{Xwp}V_\mathrm{w} + V_\mathrm{p}}}{1 + \dfrac{C_\mathrm{X}k_\mathrm{p}\bar{n}N_\mathrm{p}/\mathrm{N_A}}{k_\mathrm{X,wt}A_\mathrm{d}K_\mathrm{Xwp}}} = \frac{[X]_\mathrm{p}^\mathrm{e}}{1 + \dfrac{C_\mathrm{X}k_\mathrm{p}\bar{n}N_\mathrm{p}/\mathrm{N_A}}{k_\mathrm{X,wt}A_\mathrm{d}K_\mathrm{Xwp}}} \tag{A2}$$

where X represents the CTA; N_X is the CTA moles; K_Xdw, K_Xwp are the CTA partition coefficients between the droplets–aqueous phases, and between the aqueous–polymer phases, respectively; $\bar{n}$ is the average number of free radicals per particle; N_p is the total number of polymer particles; $\mathrm{N_A}$ is Avogadro's constant; $k_\mathrm{X,wt}$ is the CTA mass transfer coefficient across the water film covering the monomer–CTA droplets; A_d is the total monomer–CTA droplets area; and $[X]_\mathrm{p}^\mathrm{e}$ is the modifier concentration in the polymer particles under equilibrium conditions. From Eq. (A2), it is seen that: $[X]_\mathrm{p} \le [X]_\mathrm{p}^\mathrm{e}$. However, note that by increasing K_Xwp and $k_\mathrm{X,wt}$ (i.e. by increasing the CTA water solubility), $[X]_\mathrm{p}$ converges toward $[X]_\mathrm{p}^\mathrm{e}$.

Partition coefficients can be directly obtained from the literature and/or they can be measured. Thus, it is a relatively simple matter to determine $[S]_\mathrm{p}$ from Eq. (A1). In contrast, the mass transfer parameter $k_\mathrm{X,wt}$ and the evolution of the total droplets area A_d along the polymerization are generally unknown. This makes it rather difficult to estimate the product $k_\mathrm{X,wt}A_\mathrm{d}$, and therefore to apply Eq. (A2).

Appendix B. CTA feed policy of the minimum time runs

Assume a reactive CTA (i.e. with $C_\mathrm{X} > 1$). The following semibatch strategy allows to obtain any prespecified MWD in a reaction time that is close to that of an equivalent batch reaction: (i) before the polymerization start, load all of the monomer and the required amount of CTA so as to produce the required initial $\bar{M}_\mathrm{n}$ value; and (ii) along the reaction, feed the remaining CTA with the aim of producing an instantaneous MWD with the necessary $\bar{M}_\mathrm{n}$ profile. In our case, we require the instantaneously produced polymer to exhibit a constant number-average molecular weight at $\bar{M}_\mathrm{n}^\mathrm{d}$. Thus, the cumulative polymer will also exhibit a constant $\bar{M}_\mathrm{n}(t) = \bar{M}_\mathrm{n}^\mathrm{d}$. Consider the calculation of the CTA feed policy that satisfies this last objective.

Call $Q_i = \sum_{r=0}^{r=\infty} r^i [P_r]$ $(i = 0, 1)$, the first two moments of the cumulative number chain length distribution, where $[P_r]$ is the molar concentration of a dead polymer with chain length r. The number-average molecular weight of the instantaneously produced polymer is calculated from [5]:

$$\bar{M}_\mathrm{n,inst}(t) = M_\mathrm{S}\frac{\mathrm{d}(V_\mathrm{p}Q_1)/\mathrm{d}t}{\mathrm{d}(V_\mathrm{p}Q_0)/\mathrm{d}t} \tag{B1}$$

Replacing $\mathrm{d}(V_\mathrm{p}Q_1)/\mathrm{d}t$ and $\mathrm{d}(V_\mathrm{p}Q_0)/\mathrm{d}t$ by the corresponding mass balance expressions [5], the required CTA concentration in the polymer particles is given by:

$$[X]_\mathrm{p}^\mathrm{d}(t) = \frac{\dfrac{M_\mathrm{S}}{\bar{M}_\mathrm{n}^\mathrm{d}} - \dfrac{k_\mathrm{fS}}{k_\mathrm{p}}}{C_\mathrm{X}}[S]_\mathrm{p}(t) \tag{B2}$$

where k_fS is the transfer rate constant to the monomer.

The CTA molar balance may be written as follows:

$$\frac{\mathrm{d}N_\mathrm{X}}{\mathrm{d}t} = F_\mathrm{X,in}^\mathrm{d}(t) - C_\mathrm{X}k_\mathrm{p}[X]_\mathrm{p}^\mathrm{d}(t)\frac{\bar{n}(t)N_\mathrm{p}(t)}{\mathrm{N_A}} \tag{B3}$$

where $F_\mathrm{X,in}^\mathrm{d}(t)$ is the CTA molar feed rate necessary for producing $[X]_\mathrm{p}^\mathrm{d}(t)$ in the polymer particles. From the finite difference equivalent of Eq. (B3), one obtains the following recursive expression:

$$F_\mathrm{X,in}^\mathrm{d}(t + \Delta t) \cong \frac{N_\mathrm{X}(t) - N_\mathrm{X}(t - \Delta t)}{\Delta t} + C_\mathrm{X}k_\mathrm{p}[X]_\mathrm{p}^\mathrm{d}(t)\frac{\bar{n}(t)N_\mathrm{p}(t)}{\mathrm{N_A}} \tag{B4}$$

where Δt is the integration time interval.

Finally, consider the determination of $N_\mathrm{X}^\mathrm{d,0}$, or the number of CTA moles for producing $\bar{M}_\mathrm{n}^\mathrm{d}$ at $t = 0$. Applying Eq. (B2) at $t = 0$, and assuming a CTA distribution according to equilibrium, results in:

$$[X]_\mathrm{p}^\mathrm{d,0} = \frac{N_\mathrm{X}^\mathrm{d,0}}{K_\mathrm{Xdw}K_\mathrm{Xwp}V_\mathrm{d}^0 + K_\mathrm{Xwp}V_\mathrm{w}^0} = \frac{\dfrac{M_\mathrm{S}}{\bar{M}_\mathrm{n}^\mathrm{d}} - \dfrac{k_\mathrm{fS}}{k_\mathrm{p}}}{C_\mathrm{X}}[S]_\mathrm{p}^0 \tag{B5}$$

where the superscript '0' indicates initial conditions. The monomer concentrations in the polymer and aqueous phases at the start of the polymerization are given by:

$$[S]_\mathrm{p}^0 = \frac{N_\mathrm{S}^0}{K_\mathrm{Sdw}K_\mathrm{Swp}V_\mathrm{d}^0 + K_\mathrm{Swp}V_\mathrm{w}^0} \tag{B6}$$

$$[S]_{\mathrm{w}}^{0} = \frac{N_{\mathrm{S}}^{0}}{K_{\mathrm{Sdw}} V_{\mathrm{d}}^{0} + V_{\mathrm{w}}^{0}} \tag{B7}$$

Also, the initial droplets and aqueous phase volumes are, respectively:

$$V_{\mathrm{d}}^{0} = \frac{M_{\mathrm{S}}}{\rho_{\mathrm{S}}} (N_{\mathrm{S}}^{0} - [S]_{\mathrm{w}}^{0} V_{\mathrm{w}}^{0}) \tag{B8}$$

$$V_{\mathrm{w}}^{0} = \frac{V_{\mathrm{H_2O}}^{0}}{1 - \dfrac{M_{\mathrm{S}}}{\rho_{\mathrm{S}}} [S]_{\mathrm{w}}^{0}} \tag{B9}$$

where $V_{\mathrm{H_2O}}^{0}$ is the initial water volume; and ρ_{S} is the monomer density. Thus, from Eqs. (B5)–(B9), it can be concluded that:

$$N_{\mathrm{X}}^{\mathrm{d},0} = \frac{K_{\mathrm{Xwp}}(k_{\mathrm{fS}} \bar{M}_{\mathrm{n}}^{\mathrm{d}} - k_{\mathrm{p}} M_{\mathrm{S}})[M_{\mathrm{S}} N_{\mathrm{S}}^{0} K_{\mathrm{Xdw}}(1 - K_{\mathrm{Sdw}}) - \rho_{\mathrm{S}} V_{\mathrm{H_2O}}^{0}(K_{\mathrm{Sdw}} - K_{\mathrm{Xdw}})]}{k_{\mathrm{fX}}(K_{\mathrm{Sdw}} - 1) K_{\mathrm{Sdw}} K_{\mathrm{Swp}} \bar{M}_{\mathrm{n}}^{\mathrm{d}} M_{\mathrm{S}}} \tag{B10}$$

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