

## Predictive Control of Average Composition and Molecular Weight Distributions in Semibatch Free Radical Copolymerization Reactions

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**ABSTRACT:** Control of copolymer composition and molecular weight distributions is important, since they partially govern material performance. This work uses a simple but robust approach to approximate predictive control of average composition and molecular weight during free radical copolymerization, based on detailed kinetics obtained by ACOMP (automatic continuous online monitoring of polymerization reactions). Using these kinetics and elementary computations as a guide, the trends in the composition and molecular weight drifts during synthesis can be approximately controlled by predetermined, constant reagent flows into the reactor (“semibatch” operation). Two comonomer systems were chosen: one comonomer pair with very different reactivity ratios, having a tendency to high composition drift, and the other one with much closer reactivity ratios resulting in relatively constant composition during batch copolymerization. Each system had high downward molecular weight drift during synthesis, typical of free radical polymerization. Appropriate feed policies were found to control the composition and molecular weight drift tendencies at will; i.e., it was possible to keep composition constant in the first case and to increase or decrease composition in the latter, while desired trends for the average molecular weight were also obtained. The approach allows practical, approximate composition and molecular weight control in free radical copolymerization with simple reactors and pumps and without computationally intensive requirements. The results can also be useful as an Ansatz for reaction trajectory prediction and, together with the online monitoring signals, can be used for feedback controlled corrections to the reagent flows and other reaction conditions.

### Introduction

As demand for performance improvement of existing copolymers as well as new and more sophisticated materials increases, the control of composition and molecular weight distributions during the copolymerization reactions becomes more important.

Most *in situ* sensors, such as infrared (IR) and Raman scattering, primarily measure monomer conversion, not polymer molecular weight. Rheological measurements inside of reactors provide a link to polymer molecular weight, but not a direct measurement.

The lack of online measurement of polymer properties is usually the main problem in closed-loop control of polymerization reactions. For that reason many open-loop methods have been applied. The controllers employed in closed-loop methods use some online measurements, but heretofore none have continuous streams of conversion and molecular weight data available. Hence, control still heavily depends on the accuracy of available mathematical models for the input parameters. Automatic continuous online monitoring of polymerization reactions (ACOMP) allows comprehensive, model-independent monitoring of comonomer conversion, weight-average molecular weight  $M_w$ , weight-average intrinsic viscosity  $[\eta]_w$ , average composition drift and distribution, and certain measures of polydispersity.<sup>1,2</sup> ACOMP hence could provide all the necessary online measurements for closed-loop control.

There has been a significant amount of work reported on controlling composition during copolymerization reactions. The Kalman filter method is based on a linear approximation of the nonlinear process<sup>3</sup> but has problems with stability and

convergence.<sup>4–8</sup> For that reason, numerous nonlinear methods have been developed. Ellis et al.<sup>10</sup> proposed an extended Kalman filter that has been used for control purposes.<sup>7,8</sup> Nonlinear state observers that use rate of heat generation due to chemical reaction were used by Hammouri et al.<sup>3</sup> to obtain key parameters during free radical copolymerizations. These estimations and techniques are simpler to tune than Kalman filters.<sup>9,10</sup> Kravaris et al.<sup>11</sup> used temperature tracking as another nonlinear method to control copolymer composition. Model predictive control (MPC)<sup>12–16</sup> as well as nonlinear MPC (NLMPC)<sup>17–21</sup> algorithms have been suggested for control of nonlinear systems.

The semibatch approach, where policies are developed for selective reagent feeds to the reactor, has been extensively elaborated, especially for emulsion polymerization and in the context of controlling composition during copolymerization reactions.<sup>3,17,22–24,27,25,26</sup> Sun et al. developed a model based semibatch monomer feeding policies for controlled radical polymerization (CRP).<sup>27,28</sup> They provided a reactor model with mass balance equations and showed experimental results of controlling the composition. Vicente et al.<sup>29,30</sup> controlled composition and molecular weight distribution in emulsion copolymerization in an open-loop method by maintaining the ratio of comonomers. Yanjarappa et al.<sup>31</sup> synthesized, via a semibatch method, copolymers with constant composition for biofunctionalization. General semibatch policies were reviewed by Asua.<sup>32</sup>

One of the biggest issues in reactor control is the problem of nonlinearities arising during the reaction due to gelation, cage effects, exothermicity, drastic changes in kinetic coefficients (e.g., propagation and termination coefficients), etc.

While the previous work of this group focused on employing predictive control of kinetics and average molecular weight for a

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homopolymerization reaction as a first step to full feedback control based on ACOMP,<sup>33</sup> this work involves obtaining desired trends in average composition and molecular weight drift in copolymerization of two different systems.

The first system involves copolymerization of 4-vinylbenzenesulfonic acid sodium salt (hereafter VB) and acrylamide (hereafter Am), a monomer pair with quite different reactivity ratios, determined by ACOMP in this work to be  $r_{VB} = 2.14$  and  $r_{Am} = 0.18$ . This difference leads to a significant composition drift in free-radical batch copolymerization and confirms earlier work.<sup>34</sup> The aim of this portion of the work was to find a simple and robust method to obtain desired composition and molecular weight trends during reactions, including reversals of the natural batch trends, as well as to keep the drifts minimized.

The second system employs two monomers with much closer reactivity ratios, Am and [2-(acryloyloxy)ethyl]trimethylammonium chloride (hereafter Q9), for which  $r_{Q9} \approx 0.47$  and  $r_{Am} \approx 1.1$ .<sup>35</sup> Batch reactions with these comonomers resulted in low composition drift. In this portion of the work the aim was to “push” the composition drift around at will, forcing it to increase in one case and decrease in the other. There was a similar goal for the average molecular weight, i.e., to force it to increase, decrease, or remain nearly constant, as desired in each case.

## Materials and Methods

For the low drift copolymerization reactions, Am (99+%, electrophoresis grade) and Q9, 80 wt % solution in water (inhibited with 800 ppm MEHQ), and ethylenediaminetetraacetic acid tetrasodium salt hydrate 98% (EDTA, chelating agent which suppresses the effect of MEHQ) were purchased from Aldrich and used without further purification. The copolymerization reactions of Am and Q9 were initiated with potassium persulfate (99+%, ACS reagent, hereafter KPS) and were carried out in a custom-built ACOMP system. The half-life of KPS at 60 °C is 10 h.

For the high drift reactions VB was obtained from Fluka. It was copolymerized with Am and the reaction was initiated with 2,2'-azobis(2-amidinopropane) dihydrochloride (V50). V50 has a half-life of 10 h at 56 °C.

Both series of reactions were done in 0.005 mM NaCl aqueous solution in the reactor at 60 °C. Water was deionized and filtered with 0.22  $\mu$ m filter in a Modulab UF/UV system.

The principle of ACOMP and system specifics have been reported previously in detail.<sup>1,2,36</sup> The custom-built ACOMP system for most of the Q9/Am work used a two-pump, one-stage dilution with a high-pressure mixing chamber (HPMC), yielding 25-fold dilution. The dilution solvent was aqueous 0.1 M NaCl. This moderate ionic strength was chosen to largely suppress polyelectrolyte interactions and behavior in the diluted detector train solution. A Shimadzu HPLC pump was used for extraction from the reactor, and an Agilent pump was used to bring the solvent to the HPMC. The total detector flow rate was 2.5 mL/min, yielding from 0.00028 to 0.0012 g/cm<sup>3</sup> of combined monomer and polymer concentration in the detector train, depending on the experiment. Detectors comprised a Brookhaven Instruments Corp. BI-M<sub>w</sub>A (Holtville, NY) multiangle light scattering photometer (MALS), a Shimadzu RID-10A (Columbia, MD) differential refractometer (RI), a custom-built single capillary viscometer,<sup>37</sup> and a Shimadzu photodiode array SPM-20A UV/vis spectrophotometer (UV).

Another programmable Shimadzu HPLC pump was used to deliver a small stream of highly concentrated monomer solution to the reactor in the semibatch processes.

The reactor was continuously degassed with nitrogen. In order to keep the reactor temperature constant, it was immersed in an oil bath that was kept at 65 °C. The temperature in the reactor was 60 °C and monitored by a thermocouple.

Most of the VB/Am experiments used a Polymer Laboratories Ltd. ACOMP (Shropshire, UK, now part of Varian Inc.), based

on this group's instrument design and built under license from Tulane University. It used similar pumps and detector train as the custom-built one. The total dilution was 40-fold and used two mixing stages: one at low pressure and the other at high pressure. The dilution solvent was again aqueous 0.1 M NaCl. The total detector flow rate was from 2 mL/min, yielding from 0.0008 to 0.002 g/cm<sup>3</sup> of combined monomer and polymer in the detector train, depending on the experiment.

In the case of Q9-Am copolymerization, where the UV spectra of both monomers are very similar, UV wavelengths from 215 to 270 nm were used to evaluate comonomer conversion in an error minimization method previously detailed.<sup>36</sup> The ability of this method to accurately follow the conversion of each comonomer simultaneously was exhaustively evaluated in ref 36, and the method was subsequently applied to other copolymer systems.<sup>35,38–40</sup>

In the case of VB-Am copolymerization, where the spectra are quite different, two UV wavelengths were used. Am does not absorb strongly at 260 nm but VB does. At 206 nm both comonomers absorb with known extinction coefficients, so the two signals are sufficient to determine the comonomer concentrations.

After obtaining detector baselines with the aqueous solvent, the first monomer solution was added. After its baseline was stable, the second monomer was added and heated up, and once the temperature was stable the initiator was added. It was verified in separate experiments that there was no thermal polymerization in the absence of initiator.

**Free Radical Copolymerization.** In the simplest copolymerization model there are four possible propagation steps in a free radical copolymerization. Monomer 1 can be incorporated into a chain where the radical comes from the same kind of monomer (rate constant  $k_{11}$ ) or the radical can come from the other monomer (rate constant  $k_{21}$ ). Similarly, monomer 2 can be incorporated into polymer chain through a radical coming from either of the monomers (rate constants  $k_{12}$  and  $k_{22}$ ). The rate equations in this case are

$$\frac{d[m_i]}{dt} = -k_{1i}[R_1^\bullet][m_i] - k_{2i}[R_2^\bullet][m_i] = -\alpha_i[m_i] \quad (1)$$

where  $\alpha_i = k_{1i}[R_1^\bullet] + k_{2i}[R_2^\bullet]$  and  $i = 1$  or  $2$ .

The reactivity ratios are defined as

$$r_i = \frac{k_{ii}}{k_{ij}} \quad (2)$$

where  $i, j = 1$  or  $2$ , but  $i \neq j$ .

The relative change in the comonomer composition can be obtained from the Mayo–Lewis equation:<sup>41</sup>

$$\frac{d[m_1]}{d[m_2]} = \frac{[m_1](r_1[m_1] + [m_2])}{[m_2]([m_1] + r_2[m_2])} \quad (3)$$

It is hence possible to integrate eq 3 once the reactivity ratios are known, so that the composition drift can be predicted. The Mayo–Lewis model, or more sophisticated models (e.g., penultimate models), can be extended to the case where one or more reagents are flowed into the reactor in semibatch operation and the resulting equations numerically integrated to predict the composition drift.

In this work a simpler, noncomputationally intensive approach was taken to approximately predicting composition drift trends, which eliminates the use of the reactivity ratios. Thanks to continuous measurements of comonomer conversion, average instantaneous molar composition of chains being produced at each point in time were calculated from the knowledge of polymer mass created at each point.

$$F_{\text{inst},1}(t) = \frac{dm_{p1}(t)/M_1}{dm_{p1}(t)/M_1 + dm_{p2}(t)/M_2} \quad (4)$$

**Table 1. Large Reactivity Ratio Difference Reactions (Am/VB)<sup>a</sup>**

react no.	objective	VB <sub>0</sub> (%)	C <sub>VB,0</sub> (g/cm <sup>3</sup> )	C <sub>Am,0</sub> (g/cm <sup>3</sup> )	VB flow (cm <sup>3</sup> /min)	VB reservoir (g/cm <sup>3</sup> )	Am flow (cm <sup>3</sup> /min)	fractional VB drift	M <sub>w,final</sub> (g/mol)
1	batch	25	0.0186	0.0192	0	0	0	-0.25	160 000
2	reverse composition drift trend	25	0.0185	0.0191	0.459	0.1280	0	+0.21	135 000
3	keep composition constant	25	0.0186	0.0192	0.184	0.1385	0	+0.08	330 000
4	batch	15	0.0111	0.0217	0	0	0	-0.32	115 000
5	reverse composition drift trend	15	0.0113	0.0221	0.247	0.1167	0	+0.34	290 000
6	keep composition constant	15	0.0111	0.0218	0.31	0.1320	0.234	<+0.07	240 000

<sup>a</sup> All reactions were at  $T = 60$  °C, starting reactor volume was 175 mL. In all reactions  $[V50] = 0.002$  M and  $[Am] + [VB] = 0.360$  M.

**Table 2. Small Reactivity Ratio Difference Reactions (Am/Q9)<sup>a</sup>**

react no.	objective	Q9 <sub>0</sub> (%)	C <sub>Q9,0</sub> (g/cm <sup>3</sup> )	C <sub>Am,0</sub> (g/cm <sup>3</sup> )	Q9 flow (cm <sup>3</sup> /s)	Q9 reservoir (g/cm <sup>3</sup> )	Am flow (cm <sup>3</sup> /s)	Am reservoir (g/cm <sup>3</sup> )	fractional Q9 drift	M <sub>w,final</sub> (g/mol)
7	batch	50	0.019 44	0.007 11	0	0	0	0	+0.10	190 000
8	Q9 composition decrease	50	0.009 59	0.003 56	0	0	0.18	0.35	-0.35	310 000
9	Q9 composition increase	50	0.009 66	0.003 60	0.777	0.194	0	0	+0.30	35 000
10	maximal composition drift Am/Q9	0	0.000 00	0.007 11	0.78	0.194	0	0	+1.00	82 000
11	maximal composition drift Q9/Am	100	0.019 25	0.000 00	0	0	0.54	0.174	-1.00	290 000

<sup>a</sup> All reactions were at  $T = 60$  °C, starting reactor volume was 340 mL. In all reactions  $[KPS] = 0.00167$  M and  $[Am] + [Q9] = 0.100$  M, except in reaction 7  $[Am] + [Q9] = 0.200$  M.

where  $M_1$  and  $M_2$  are the molar masses of monomers 1 and 2, respectively, and the polymer mass increments  $dm_{p1}$  and  $dm_{p2}$  are computed from the derivatives of ACOMP data for each comonomer concentration according to

$$m_{p,i}(t) = [c_{t,i}(t) - c_{m,i}(t)]V(t) \quad (5)$$

where  $i = 1$  or 2. The total concentration (including monomer and polymer) of each component  $c_{t,i}$  is approximately given by

$$c_{t,i}(t) \approx c_{m,i}(0) + \frac{Q_{m,i}c_{m,i}'t}{V_0 + (Q_{m,i} - q)t} \quad (6)$$

The  $c_{m,i}(t)$  are measured directly from the ACOMP UV diode array data in this work.

#### Semibatch Operation: Constant Monomer Flow to the Reactor.

**Homopolymerization.** As shown in previous work, a constant monomer flow at rate  $Q_m$  (in cm<sup>3</sup>/s) can be a powerful means of controlling molecular weight in case of free radical homopolymerization. The molar monomer concentration in this case is

$$\frac{d[m]}{dt} = -[m](\alpha_{hp} + \frac{Q_m}{V(t)}) + \frac{[m]'}{V(t)}Q_m \quad (7)$$

where  $\alpha_{hp} = k_{p}[R^*]$  is the homopolymerization rate coefficient.  $V(t)$  is the total volume in the reactor and is given by

$$V(t) = V_0 + (Q_m - q)t \quad (8)$$

where  $q$  is the reactor extraction rate via the ACOMP “front end”.

The concentration of monomer in the reservoir can be made high enough that only a low flow rate  $Q_m$  is needed so that relatively little increase of  $V_0$  occurs during the reaction (<10%). In this work the reservoir concentration of the monomer pumped to the reactor was typically 10 times the initial reactor concentration. In this case  $V(t) \approx V_0$ .

Solving eq 5 with that condition yields

$$[m](t) = [m]_0 \exp\left\{-\left(\frac{Q_m + \alpha_{hp}V_0}{V_0}\right)t\right\} + \left(\frac{[m]'}{Q_m + \alpha_{hp}V_0}\right)\left(1 - \exp\left\{-\left(\frac{Q_m + \alpha_{hp}V_0}{V_0}\right)t\right\}\right) \quad (9)$$

This expression shows that a quasi-steady state plateau (“quasi” since  $V(t)$  is not strictly constant, but only slowly changing) with a time scale of  $V_0/(Q_m + \alpha_{hp}V_0)$ . The polymer concentration  $[m]_p$  was found from the concentration change of combined polymer and monomer  $[m]_t$

$$\frac{d[m]_t}{dt} = -[m]_t \frac{Q_m}{V(t)} + \frac{[m]'}{V(t)}Q_m \quad (10)$$

$$[m]_p(t) = [m]_t(t) - [m](t) \quad (11)$$

The special case of keeping monomer concentration and hence molecular weight constant for homopolymers was investigated, and the following monomer feed condition was found:

$$Q_m = \frac{\alpha_{hp}V_0[m]_0}{[m]' - [m]_0} \quad (12)$$

A qualitative adaptation of the above approach is used here to provide very simple, but robust, predictive estimates of composition and molecular weight drift during semibatch free radical copolymerization.

## Results

Table 1 summarizes experiments with Am/VB, which have large differences in reactivity ratios. Table 2 gives a summary of experiments with Am/Q9, which have low reactivity ratio differences. The objective of each experiment is also given in the tables.

Figure 1 shows typical raw data for a semibatch reaction, no. 8 in Table 2, which are more complex than typical ACOMP data for batch free radical copolymerization reactions. The RI signal increases throughout the reaction, showing that the sum of monomer and copolymer is increasing continuously ( $dn/dc$  of the copolymers are only slightly larger than the  $dn/dc$  values of their corresponding monomers). The increasing light scattering and viscosity signals show continuous increase in the concentration of polymer in the reactor, and the upward inflection of the light scattering halfway through the reaction shows the effect of increasingly Am-rich copolymers on  $M_w$  (see below). The initial decrease of UV shows that the conversion of both monomers decreases  $[Am]$  more quickly than the constant inflow rate increases  $[Am]$ . It was found previously<sup>33</sup> that  $\alpha_{Am}$  decreases as



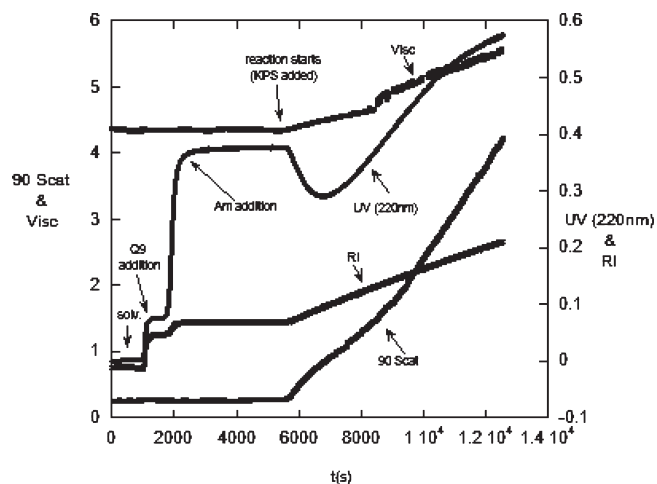


Figure 1. Typical raw data for a semibatch reaction (reaction 8).

the ratio of  $[Q9]/[Am]$  decreases. Hence, when  $[Q9]/[Am]$  decreases, due to Am inflow, the Am conversion rate slows and  $[Am]$  increases more due to inflow than it decreases due to the reaction, and so the net UV signal eventually stops decreasing and begins to increase. Also, since the polymer itself absorbs/scatters some UV light, some of the continued increase in the UV signal is due to this, especially at later stages of the reaction when the polymer concentration is high. The goal of reaction 8 was to make  $F_{inst,Q9}$  decrease during the reaction. In a batch reaction of similar starting conditions  $F_{inst,Q9}$  would normally increase somewhat (see below).

In both the VB/Am and Q9/Am reactions the conversion of each comonomer could be approximately fit with an exponential (first order) time dependence. The first-order rate constants are used below as part of the simplifying assumptions used to carry out the approximate predictive control.

**I. Large Difference in Reactivity Ratios: VB-AMD Copolymerization.** Two series of experiments at different starting VB-Am ratios were performed, one series with 25% molar starting VB (reactions 1, 2, and 3), and the second series with 15% molar starting VB (reactions 4, 5, and 6).

*i. Pure Batch Reactions.* First, pure batch VB-Am copolymerization reactions were performed (reactions 1 and 4) to provide the basic rate coefficients necessary for semibatch feed calculations. The pure batch equations apply if the only flow during the experiment is the ACOMP extraction flow rate  $q$  from the reactor.

$$[m_i] = [m_i]_0 \exp(-\alpha_i t) \quad (13)$$

For reaction 1, performed at 25% of VB at  $t = 0$ , assumed first-order fits to the concentration data gave exponential rate coefficients for both comonomers of  $\alpha_{VB,1} = 0.00033$  [1/s] and  $\alpha_{Am,1} = 0.0002$  [1/s]. Total fractional composition drift, given by  $\Delta F_{inst,VB} = F_{inst,VB,final} - F_{inst,VB,0}$ , was  $-0.25$ . For reaction 4, performed at 15% starting VB at  $t = 0$ , the rate coefficients were found to be  $\alpha_{VB,2} = 0.00036$  [1/s] and  $\alpha_{Am,2} = 0.00015$  [1/s].  $\Delta F_{inst,VB}$  was  $-0.32$ . These rate values are used accordingly in subsequent semibatch feed calculations for the 15% and 25% of VB experiments.  $F_{inst,VB}$  vs  $t$  for the two reactions is shown in Figure 2.

**Series 1–25% Starting VB.** *ii. Using Semibatch to Reverse Copolymer Drift Compared to Batch Case.* In the previous work, a semibatch feed policy was found to keep monomer concentration constant, which resulted in constant weight-average molecular weight  $M_w$  during a homopolymerization reaction. The monomer inflow equation satisfying that condition is given by eq 10. The same feed policy was implemented in reaction 2 for the

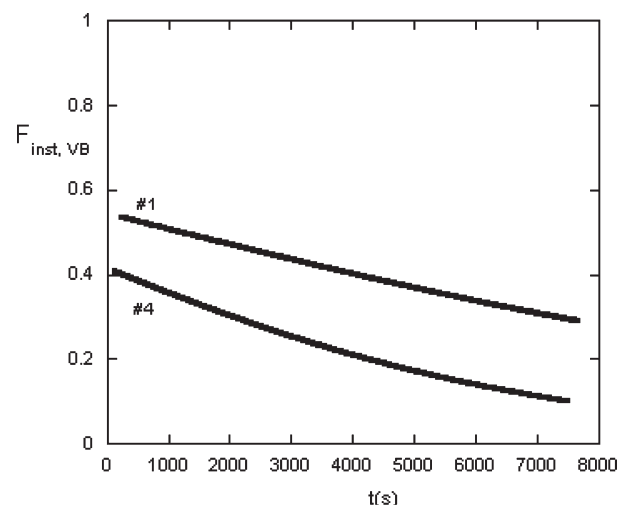


Figure 2. Composition of VB vs  $t$  for batch reactions 1 and 4.

faster reacting VB monomer. VB was flowed into the reactor at 0.459 mL/min. The concentration of the VB reservoir was 0.141 g/mL, and the flow rate was obtained from eq 10. The comonomer concentrations in the reactor and the resulting  $F_{inst,VB}$  are shown in Figure 3a,b.

It was not expected that this procedure would keep VB constant, since the concentration of each comonomer influences its own as well as the other comonomer's reaction rate, but it was nonetheless expected that VB would come to dominate over the depleting Am, thus driving the composition drift toward increasing VB. The resulting VB composition did, in fact, drift upward (Figure 3b), with a total fractional composition drift, of  $\Delta F_{inst,VB} = +0.21$ , less in magnitude and opposite in sign from the corresponding batch reaction (reaction 1).

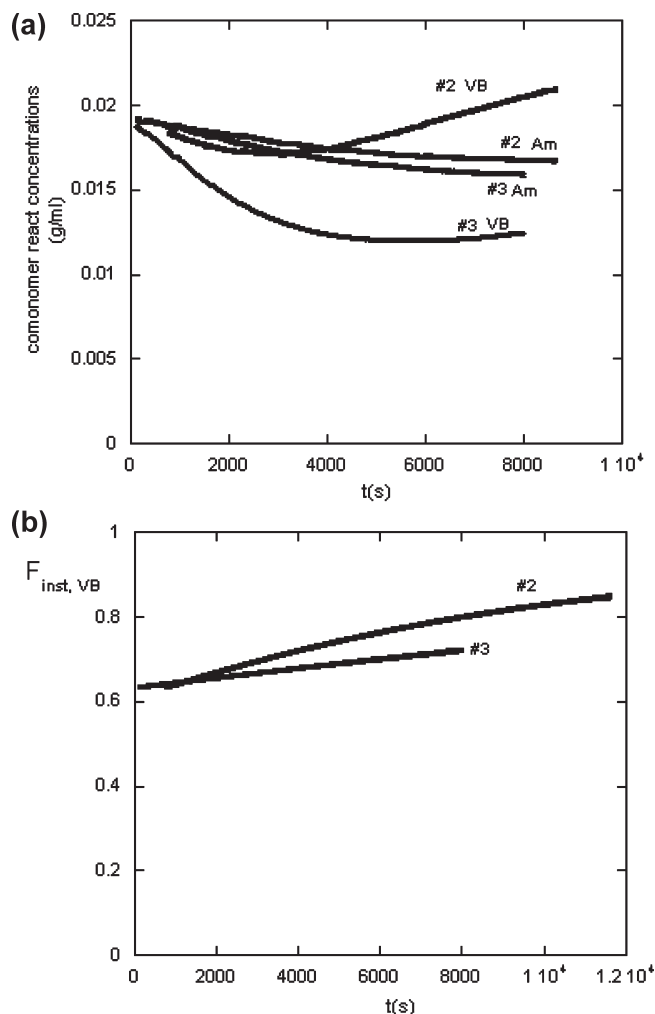
*iii. Using Semibatch To Keep Monomer Ratio Constant.* In order to keep the composition constant, the ratio of comonomers must stay constant during the reaction, i.e.

$$\frac{d\left(\frac{[m_{VB}]}{[m_{AMD}]}\right)}{dt} = 0 \quad (14)$$

Solving eq 14, using eq 5 and taking the case where VB is the only monomer flowing into the reactor, the following formula for the monomer inflow was obtained:

$$Q_{VB} = \frac{[m_{VB}]V_0(\alpha_{VB} - \alpha_{Am})}{[m'_{VB}]} \quad (15)$$

In semibatch reaction 3, the starting comonomer and initiator concentrations were the same as reaction 2. However, in the flow rate eq 15, monomer concentration changes during the reaction; hence, the ideal flow rate of the monomer to the reactor should change as well. Nonetheless, using a simple pump with only fixed flow rates available, a constant flow of monomer was used to achieve an approximate result. The rate was obtained from eq 15, but constant  $[m_{VB}] = [m_{VB,0}]$  was used. As seen in Figure 3a, VB concentration decreased then increased slightly during the rest of the reaction, so the flow rate was somewhat overestimated. As a result VB composition, shown in Figure 3b, increased somewhat during the reaction. The results, while not giving a perfectly steady composition nonetheless yield a drift of only  $\Delta F_{inst,VB} = +0.08$ . Dual monomer feed experiments below provide a better approach to minimal composition drift.



**Figure 3.** (a) Reactor concentration of VB and Am vs  $t$  for semibatch reactions 2 and 3. (b) Composition of VB vs  $t$  for semibatch reactions 2 and 3.

**Series 2–15% of VB.** *iv. Using Semibatch To Reverse Composition Drift, but at Lower Starting  $[VB]_0/[Am]_0$ .* In reaction 5, similarly to reaction 2, eq 3 with  $[m_{VB}] = [m_{VB,0}]$  was used to calculate the flow rate. The results are shown in Figure 4a,b. A high positive drift was obtained in this way; total drift was  $\Delta F_{inst,VB} = +0.34$ , comparable to batch, although in the opposite direction; i.e., these conditions led to a complete reversal of the natural drift of the batch system in the opposite direction of increasing VB.

*v. Using Dual Feed; Each Monomer Flowed into Reactor Using Separate Pumps.* In order to keep the composition constant using a constant monomer inflow, the concentration of both comonomers has to stay constant during the reaction, i.e.

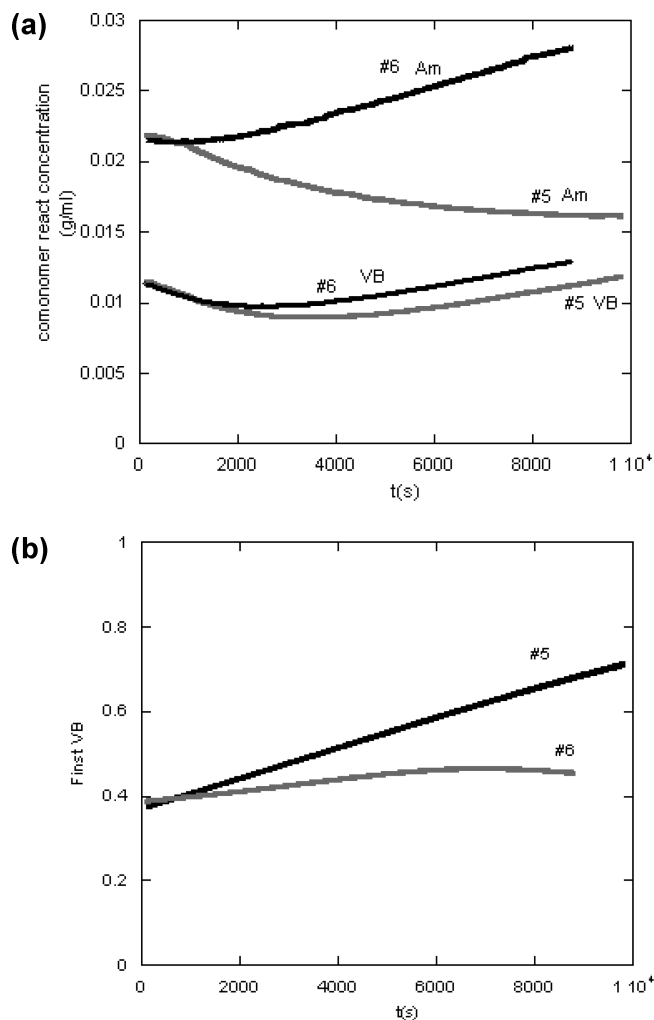
$$\frac{d[m_{VB}]}{dt} = \frac{d[m_{Am}]}{dt} = 0 \quad (16)$$

Solving eq 16 provided the following monomer feed rate equations:

$$Q_{VB} = \frac{V_0[m_{VB}]\alpha_{VB}}{[m'_{VB}] - [m_{VB}]_0} \quad (17a)$$

$$Q_{AMD} = \frac{V_0[m_{Am}]\alpha_{Am}}{[m'_{Am}] - [m_{Am}]_0} \quad (17b)$$

The conditions (17a) and (17b) were implemented in reaction 6. VB, at concentration = 0.132 g/mL, was flowed to the

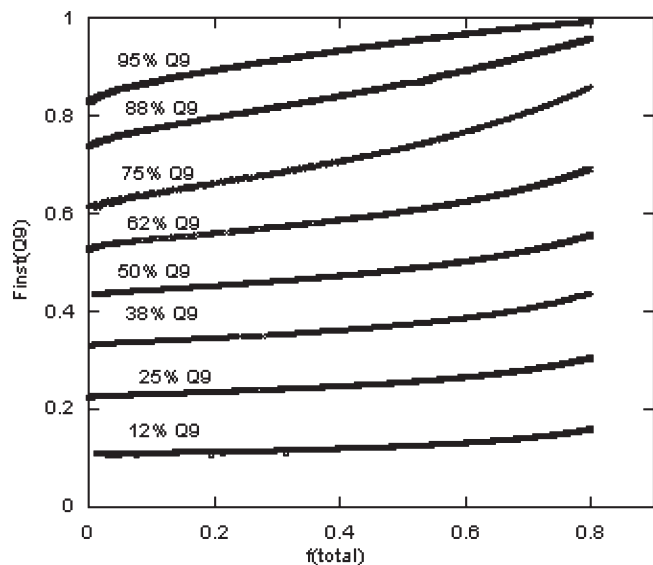


**Figure 4.** (a) Reactor concentration of VB and Am vs  $t$  for semibatch reactions 5 and 6. (b) Composition of VB vs  $t$  for semibatch reactions 5 and 6.

reactor at constant feed = 0.31 mL/min, and Am, at concentration = 0.143, was flowed separately at constant feed of 0.234 mL/min. The results are shown in Figure 4a,b. There was some drift in reactor concentration of both comonomers, but the resulting composition was held reasonably constant, and the total drift in  $F_{inst,VB}$  was less than 7%.

In order to have even better control of the composition, one needs to have programmable pumps whose flows can be adjusted by feedback from the detectors. It was shown, however, that even with simple pumps a good approximation to constant composition can be achieved.

**II. Small Difference in Reactivity Ratios: Q9-Am Copolymerization.** *i. Pure Batch Reactions.* Similarly to VB-Am semibatch copolymerization series, pure batch Q9-Am copolymerization reactions were performed first. Figure 5 shows the composition changes for the whole series of batch reactions. Because of the similar reactivity ratios of Q9 and Am ( $r_{Q9} \approx 0.47$  and  $r_{Am} \approx 1.1$ ), there is not much composition drift in any of the reactions. The first series of semibatch reactions (reactions 8–10) contained 50% of Q9 at the beginning of the reaction; hence, rate coefficients from batch reaction 7, which had the same starting reaction conditions, were used to obtain desired semibatch feed policies. The monomer feed was calculated, in each case, from eq 12. The rates from reaction 7 are  $\alpha_{Q9} = 0.00074$  [1/s]



**Figure 5.** Composition drift for a series of Q9-Am batch copolymerizations.

and  $\alpha_{Am} = 0.0001$  [1/s]. As mentioned above, it was found that  $\alpha_{Am}$  decreases as the ratio of [Q9]/[Am] decreases.<sup>33</sup>

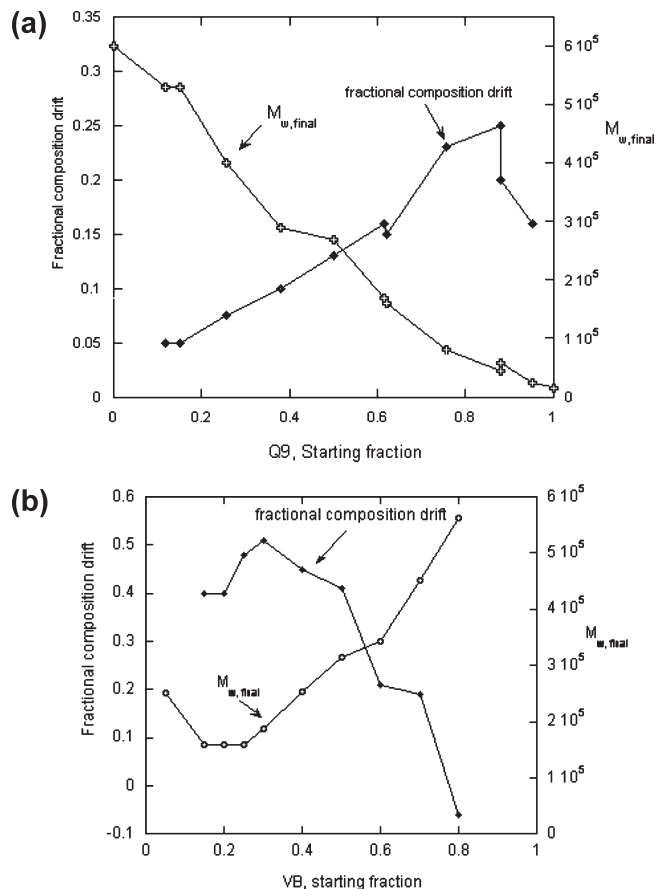
Figure 6a shows how markedly both fractional composition drift (albeit low) in Q9 and final  $M_w$  are influenced by the starting fraction of Q9;  $M_{w,final}$  decreases strongly with increasing starting fraction of Q9, whereas composition drift increases and reaches a maximum of 0.25 at 0.90 starting Q9. These data serve as a guide for achieving predictable changes in molar mass and composition in the following semibatch experiments.

Figure 6b shows the remarkable contrast in the  $M_w$  trend when VB is substituted for Q9 as the comonomer;  $M_w$  increases strongly and composition drift decreases strongly with starting fraction of VB, contrary to the Q9/Am case.

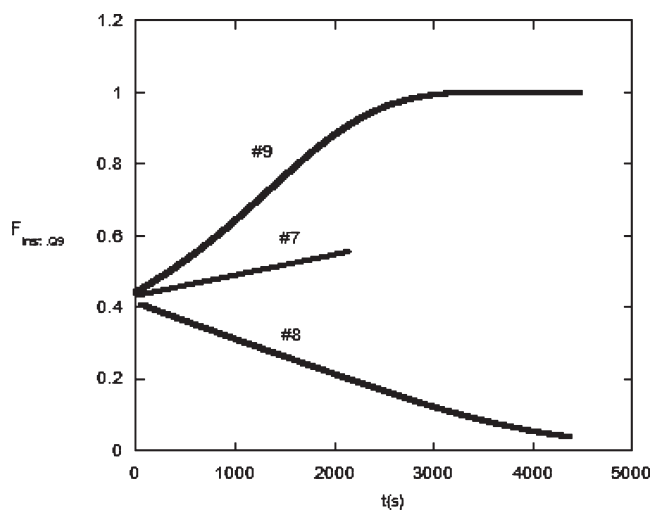
*ii. Semibatch Reactions To Decrease Q9 Composition.* Reaction 8 was performed with the purpose of decreasing Q9 composition. Am was fed to the reactor at 0.18 mL/min, and the concentration of Am reservoir was 0.35 g/mL. The resulting composition is shown in Figure 7. As desired, it decreased significantly and monotonically in time during conversion.

*iii. Semibatch Reactions To Increase Q9 Composition.* Reaction 9 was performed to increase Q9 composition. Q9 was flowed to the reactor at 0.777 mL/min. The concentration of the reservoir was 0.194 g/mL. As desired Q9 composition increased. The increase was monotonic, but Am was depleted quite early in the reaction and roughly after 2500 s the copolymerization transformed to a homopolymerization. The result is shown in Figure 7.

*iv. Maximal Composition Drift (Am/Q9).* In reaction 10 the initial conditions were changed. There was only pure Am in the reactor before the reaction started. Q9 was flowed to the reactor after the reaction had been initiated. When computing the feed rate, the same reaction rates were used as in the previous three experiments. The resulting composition is shown in Figure 8 where the initial condition of  $[Q9](t=0) = 0$  ensures 100% pAM at the very beginning of the reaction, and the initial  $F_{inst,VB}$  was set to zero to ensure this. As desired Q9 composition increased and Am was fully depleted at the end of the reaction. Strikingly, it was possible to drive the reaction from pure Am homopolymer at  $t=0$  to pure Q9 homopolymer at  $t=6500$  s, with all intermediate compositions being produced during the reaction.



**Figure 6.** (a)  $M_{w,final}$  and total fractional composition drift vs starting fraction of Q9/Am batch reactions ( $[Am] + [Q9]/[KPS] = 120$ ). (b)  $M_{w,final}$  and total fractional composition drift vs starting fraction of VB/Am batch reactions ( $[Am] + [VB]/[V50] = 180$ ).



**Figure 7.** Composition of Q9 vs  $t$  for semibatch reactions 8 and 9.

*v. Maximal Composition Drift (Q9/Am).* In reaction 11, only Q9 was present in the reactor at  $t=0$ , and Am was flowed into the reaction once the reaction had been initiated. The resulting composition is shown in Figure 8. Again, the initial condition that  $[Am]=0$  ensures  $F_{inst,VB} = 1.00$  at  $t=0$ . The reaction was hence driven from pure pQ9 at the outset to pure pAm toward the end, with all intermediate compositions synthesized in the reaction.

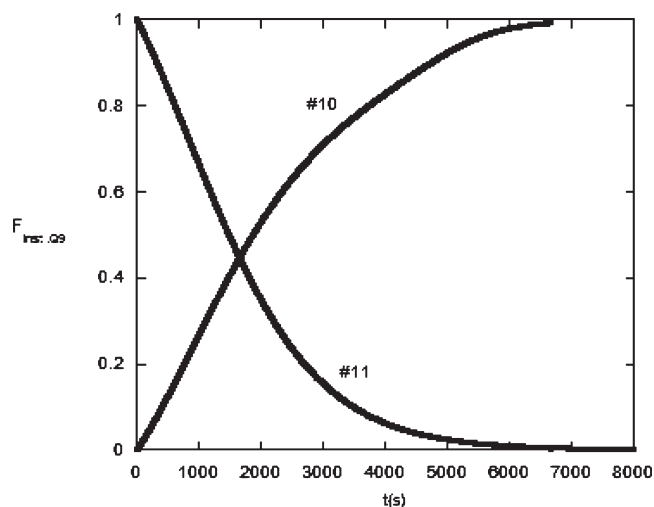


Figure 8. Composition of Q9 vs  $t$  for semibatch reactions 10 and 11.

**Molecular Weight Control by Semibatch.** The results of  $M_w$  for VB/Am and Q9/Am copolymerizations are shown in parts a and b of Figure 9, respectively. The  $M_w$  drift for some batch copolymerizations of Q9 and Am is also shown. In all batch reactions  $M_w$  tends downward during conversion, as is typical in free radical polymerization where chain transfer reactions are negligible.

$M_w$  is not only affected by the composition but also by the starting comonomer fraction in the reactor. As seen in Figure 6a, Am yields higher masses whereas increasing Q9 yields smaller masses. In contrast, Figure 6b shows how  $M_w$  decreases with increasing Am and increases with VB in the VB/Am reactions.

In the case of VB/Am copolymerization,  $M_w$  can be kept constant either by decreasing Am concentration during the reaction (for example, by not feeding it) and by an appropriate increase in VB composition (by feeding it) or by feeding both comonomers to keep both of their concentrations constant. Semibatch reactions 3 and 5 were flooded with VB, and hence the composition increased but Am concentration decreased (since it was not fed). This led to a relatively constant  $M_w$ , as seen in Figure 9a.

An attempt to control  $M_w$  by keeping both comonomer concentrations concentration was implemented in reaction 6.  $M_w$  increased a small amount due to the fact that the reactor was slightly flooded with both comonomers; however, the constancy of  $M_w$  is quite good.

In the case of Q9/Am copolymerization predictions of the trend in  $M_w$  could be made by reference to Figure 6a. In order to decrease  $M_w$  by a greater percentage than usual during the reaction, Q9 was fed into the reactor. Semibatch reaction 9 involved Q9 feed and resulted in a large decrease in  $M_w$ , as seen in Figure 9b. The fractional decrease in  $M_w$  is much greater than the corresponding decrease in  $M_w$  from a similar batch reaction (also shown in Figure 9b).

In reaction 10 a maximal increase in Q9 upward composition drift was sought, and this leads to a corresponding very large decrease in  $M_w$ .  $M_{w,0}$  is much larger for reaction 10 than for reaction 9, as expected from Figure 6a, where higher Am yields higher  $M_w$ . Reaction 10 started with pure Am and was then fed with Q9.

According to Figure 6a, feeding Am into the reactor should result in an increase of  $M_w$  during the reaction. Reaction 8 involved Am flow, and there is a dramatic increase in  $M_w$ , seen in Figure 9b. Reaction 11, involving maximal increase in upward composition of Am, gives an

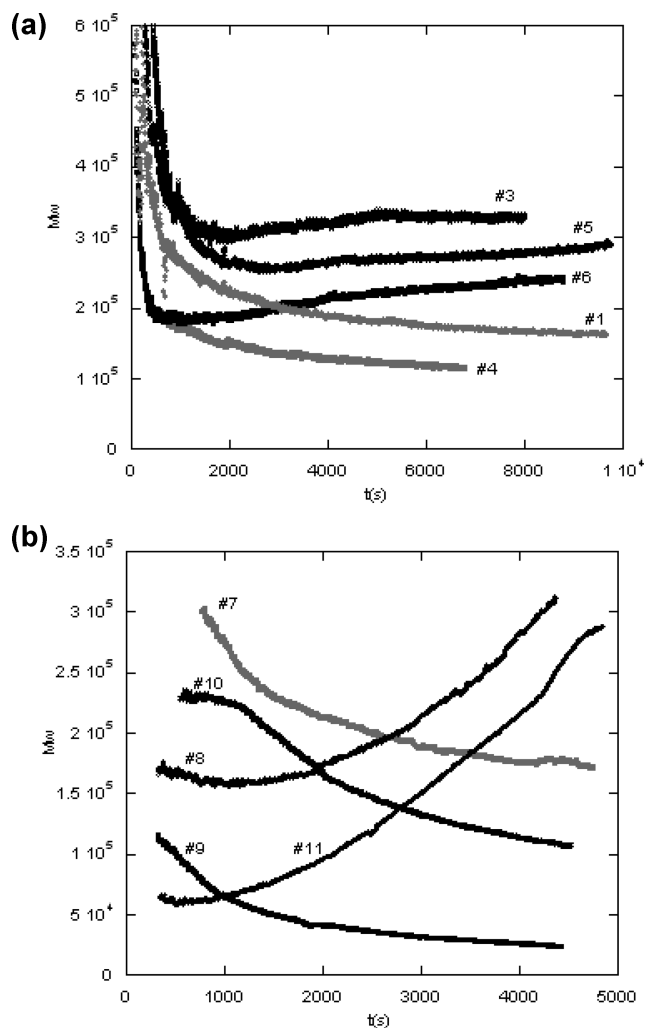


Figure 9. (a) Average molecular weight for VB-Am semibatch copolymerization. (b) Average molecular weight for Q9-Am semibatch copolymerization. Note that reaction 7 had twice as much [monomer]/[initiator] than the other reactions.

even more dramatic increase in  $M_w$ , since starting with pure Q9 yields a lower starting  $M_w$ .

## Conclusion

A simple way of approximately controlling composition and  $M_w$  without use of reactivity ratios and intensive computations and with a basic reactor and constant flow rate feed pumps was presented in the case of two distinct free radical copolymerizations, one in which reactivity ratios were widely different, leading to large composition drift in batch reactions, and the other one in which reactivity ratios were similar, and little drift occurred in batch reactions.

It was shown that by appropriate monomer feed to the reactor, of one or both monomers, the batch trends can be modulated at will and even be reversed from their natural batch reaction trends. It was possible to program the feed rates so that increases, decreases, and minimal changes in composition and  $M_w$  could be achieved. This type of trend-based estimation of reaction trajectory is a simple but effective means to yield good results for synthesizing copolymers of desired average composition and molecular weight. While achieving an approximate level of control over composition and molecular weight in copolymerization reactions may often be sufficient, this approach could also

be used to establish Ansatz conditions for reactions to produce on-command polymers, where automated feedback control can be implemented based on the massive ACOMP detector data stream. In this latter case much more precise reaction control could be achieved.

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