Copolymer Composition Control Policies: Characteristics and Applications

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Characteristics of three classes of copolymer composition control policies are presented and discussed with applications on several typical copolymer systems at the simulation stage. The effects of these policies are shown on polymerization rate, copolymer composition, and molecular weight, branching and sequence length properties. Extensions to terpolymerizations (and hence, other multi-component polymerizations) are also modeled and presented. Generalized procedures for practical implementation and comparisons among policies are highlighted, and special cases of these policies are investigated.

Keywords: copolymer composition; copolymerization; terpolymerization; composition control policies; free radical polymerization; gradient block copolymers

1 Introduction

Today many polymers with novel properties are composed of two or more monomer species (copolymers or terpolymers; in general, multi-component polymers). The properties of these copolymers are determined by many factors, such as monomer type, molecular weight and architecture, sequence length and copolymer composition. Evidently, it is very important to control or optimize copolymer properties in order to develop improved polymer products. In order to control copolymer properties, it is necessary to control all the factors mentioned above. Among them, copolymer composition has a great impact on copolymer properties, because it can directly affect the microstructure of the copolymer (whereas the microstructure in its turn influences other application properties in several ways). Therefore, controlling copolymer composition can be regarded as an important technique in developing improved polymer products.

Still, these days, most of research laboratory screening (exploratory) experiments are conducted using a batch type reactor and the usual way of manipulating copolymer composition is by changing initial monomer feed composition (herein and in the remainder of the discussion, the concepts referring to (binary) copolymer composition and other characteristics can be extended to include terpolymers and other multi-component cases). However, for all batch copolymerizations (except for azeotropic copolymerizations), the compositions of the initial comonomer feed and of the copolymer chains are always different. The comonomer composition in the reactor changes as one of the monomers preferentially enters the copolymer. Thus, there is a drift in monomer composition in the reactor toward the less reactive monomer as the degree of conversion increases. This results in a parallel variation of copolymer composition with conversion. Basic details of copolymerization and composition drift can be found elsewhere (1, 2).

Using a semi-batch (semi-continuous, including an intermittent) feed is one of the practical solutions to avoid copolymer composition drift. Monomer(s) can be fed to the reactor in a semi-batch mode to keep monomer composition in the reactor constant (or almost constant) during polymerization. Using a semi-batch process to control copolymer composition is not a new idea (see, for instance, Odian (1) and Dotson et al. (2) for the basic principle, and further illustrations when translated into copolymer composition control policies (with applications) in Hamielec et al. (3) and Dubé et al. (4)). However, detailed characteristic features of composition control policies, procedures for practical implementation and comparisons among policies have not been investigated widely. Therefore, one of the main aims of this work is to investigate characteristic features of these policies and offer further insights by comparing these policies. Extensions to terpolymerization (and thus, general multicomponent cases) will

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also be shown. Recently, an interesting class of materials, gradient copolymers (with their chemical composition varying continuously along a certain segment of the polymer chain) have been the subject of research work (5, 6). The structure of a gradient copolymer is best described as being between two extremes, namely between the corresponding diblock copolymer and a random copolymer, and thus it has been predicted that thermal and other properties of a gradient copolymer should deviate from those of random or diblock copolymers (7). Semi-batch processes can also be applied to the production of gradient copolymers. With a semi-batch feed, it is possible to produce a copolymer with the desirable gradient in its gradient block. The procedure to determine the monomer feed rate needed to produce a desired gradient is also investigated and an example given in this paper.

2 Background

In the absence of an azeotrope and when one monomer is more reactive than the other in a binary, batch copolymerization (say, with reactivity ratios $r_1 > 1$ and $r_2 < 1$), the instantaneous copolymer composition will decrease in monomer 1 with an increase in monomer conversion. The extent of compositional drift which leads to a copolymer heterogeneous in composition depends on the ratio of reactivity ratios r_1/r_2 (increases with an increase in r_1/r_2), the initial monomer composition (initial mole fraction of free, unreacted monomer 1, f_{10}), and the monomer conversion (x). A copolymer which is heterogeneous in composition usually has inferior mechanical/optical application properties, and therefore industrial semi-batch processes have been developed to reduce compositional heterogeneity.

Two basic feed policies were introduced (3, 4) and other variations of these policies were developed previously (8–22). Theoretically, many kinds of feed policies are possible. Effective commercial processes are usually based on one or a combination of these feed policies. From a practical point of view, these feed policies can be summarized in three categories, and are discussed briefly below.

2.1 Semi-Batch Feed Policies

The three feed policies are schematically shown in Figure 1. N_1, N_2 are moles of monomers in the reactor (mol), M_1, M_2 are concentrations of monomers (mol/L), $F_{1,in}, F_{2,in}$ are monomer feed rates (mol/min), R_{P1}, R_{P2} are net rates of monomer disappearance by reaction (mol/L/min), and V is the reacting volume of the polymerizing mixture in the reactor (L).

(Policy 1, Figure 1). All of the slower monomer and a sufficient amount of the faster monomer (to give the desired copolymer composition F_1) are added to the reactor at time zero. Thereafter, only the faster monomer is fed to the reactor with a time-varying feed rate to maintain N_1/N_2 (the ratio of the number of moles of monomer 1 to that of monomer 2 in the reactor) and hence F_1 constant with time or conversion.
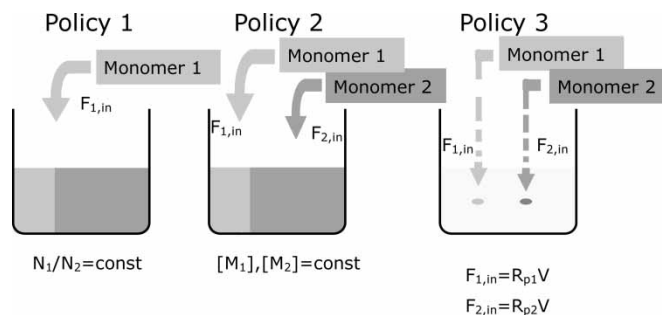

Fig. 1. Schematic depiction of semi-batch feed policies.

(Policy 2, Figure 1). Monomers 1 and 2 at the desired concentration levels (to give the desired F_1) are added to the reactor at time zero. Thereafter, both monomers 1 and 2 are fed to the reactor with time-varying feed rates to maintain M_1, M_2 and therefore F_1 constant with time or conversion.

(Policy 3, Figure 1). Monomers 1 and 2 at the desired concentration levels (to give the desired F_1) are added to the reactor at time zero. Thereafter, both monomers 1 and 2 are fed to the reactor at exactly the same rate as the consumption (propagation) rate, R_{P1} and R_{P2}, in order to maintain N_1, N_2 and hence, F_1 constant with time or conversion.

According to these three policies above, the monomer inflow rate is, in general, a function of propagation rate constants (i.e., reactivity ratios), monomer concentrations and the total radical concentration. Hence, in order to calculate the optimal monomer feed policy in order to control the polymerization rate that will yield constant copolymer composition, the total radical concentration must be specified in advance and kept at a specific constant value. This may be accomplished through either an initiator feed policy or a heat production policy, in order to keep the total radical concentration constant through the polymerization. Even further, the practical implementation of monomer feed policies requires the use of on-line (or possibly off-line) measurements to permit one to adjust for uncontrolled variations in recipe impurities (such as oxygen and other radical scavengers), which can affect radical concentration. One can thus in principle implement a practical calorimetric control of monomer feed, and obtain eventually, for any monomer feed policy, a relationship between the instantaneous heat generation rate (related to the rate of polymerization, i.e., rate of incorporation of monomers in the copolymer) and the monomer molar feed (inflow) rate.

In addition, since the three policies exhibit in principle different monomer concentration profiles in the reactor (these characteristics will become evident later in the discussion), molecular weight and branching/crosslinking levels will differ from policy to policy. Thus, there will be different advantages and disadvantages associated with each policy, considering both productivity and polymer quality. Put differently, the evolution of polymer properties other than copolymer composition during these semi-batch policies may be highly dependent on both reactor operating conditions and specific recipe.

2.2 Mathematical Model

The equations to be solved to determine the required monomer feed rates to produce a compositionally homogeneous binary copolymer in a semi-batch process are cited below.

$$\frac{dN_1}{dt} = F_{1,in} - R_{P1}V \tag{1}$$

$$\frac{dN_2}{dt} = F_{2,in} - R_{P2}V \tag{2}$$

$$R_{P1} = -N_1(k_{11}\phi_1 + k_{21}\phi_2)[R\cdot] \tag{3}$$

$$R_{P2} = -N_2(k_{12}\phi_1 + k_{22}\phi_2)[R\cdot] \tag{4}$$

$$\frac{dV}{dt} = \frac{F_{1,in}MW_1}{\rho_{m1}} + \frac{F_{2,in}MW_2}{\rho_{m2}}$$
$$- \left[R_{P1}MW_1\left(\frac{1}{\rho_{m1}} - \frac{1}{\rho_P}\right) \right.$$
$$\left. + R_{P2}MW_2\left(\frac{1}{\rho_{m2}} - \frac{1}{\rho_p}\right) \right]V \tag{5}$$

where (for the additional symbols used above): k_{ij} propagation rate constant for radical ending in monomer i adding monomer j (L/mol/sec); ϕ_i mole fraction of radical ending in monomer i;

$$\phi_1 = \frac{k_{21}f_1}{k_{12}f_2 + k_{21}f_1}$$
$$\phi_2 = 1 - \phi_1$$

f_i molar fraction of ith-monomer (unreacted, unbound); $[R\cdot]$ total radical concentration (mol/L); MW_i molecular weight of monomer i (g/mol); ρ_m density of monomer (kg/L); ρ_p density of polymer (kg/L); t time.

Conditions to be satisfied for the three policies, respectively:

Policy 1:

$$\frac{d}{dt}\left(\frac{N_1}{N_2}\right) = 0 \; \frac{dN_1}{dt} = \left(\frac{N_1}{N_2}\right)\frac{dN_2}{dt} \tag{6}$$

$$F_{2,in} = 0 \tag{7}$$

Policy 2:

$$\frac{dN_1}{dt} = [M_{10}]\frac{dV}{dt} \tag{8}$$

$$\frac{dN_2}{dt} = [M_{20}]\frac{dV}{dt} \tag{9}$$

Subscript zero above denotes initial monomer concentration.

Policy 3:

$$F_{1,in} = R_{P1}V \tag{10}$$

$$F_{2,in} = R_{P2}V \tag{11}$$

If the volume shrinkage caused by the difference between monomer and polymer densities is small enough to be negligible compared to the volume change caused by the monomer feed, Equations (1−5) and (8, 9) can be solved analytically, and one can show that the mole fraction of monomer in the feed stream is kept constant during polymerization. This means that if monomers are pre-mixed at the desired concentration, only one feed stream is needed. However, in general, the mole fraction of monomer in the feed stream is different from the target composition. Therefore, it is necessary to calculate the desired mole fraction of monomer in the feed stream beforehand.

In contrast, the mole fraction of monomer in the feed stream becomes equal to the instantaneous copolymer composition in policy 3, because:

$$\frac{F_{1,in}}{F_{1,in} + F_{2,in}} = \frac{R_{P1}V}{R_{P1}V + R_{P2}V} = F_{1,inst} \tag{12}$$

Therefore, the composition of the feed stream can be set to the same composition as the target copolymer composition (to be held constant throughout polymerization). However, also in policy 2, if monomer concentrations are kept sufficiently low, the mole fraction of monomer in the feed stream becomes equal to the instantaneous copolymer composition. When M_1 and M_2 are close to zero, N_1 and N_2 are also nearly zero. Therefore, the relationship $F_{1,in} = R_{p1}V$ and $F_{2,in} = R_{p2}V$ can be considered valid in policy 2, as well. Hence, policy 3 can be viewed as a special case of policy 2.

Since it is not always possible to obtain analytical solutions, all calculations were conducted (in the general case) numerically using MATLAB. The calculation procedure contains four steps:

1. Start with an assumed $F_{1,in}$ and $F_{2,in}$
2. Calculate N_1, N_2 and V using some numerical technique for solving ordinary differential equations (say, a 4th order Runge-Kutta method)
3. Evaluate specific policy conditions (see Eqs (6−11))
4. Modify $F_{1,in}$ and $F_{2,in}$

Steps 1−4 are repeated iteratively until the appropriate conditions are satisfied. Function fsolve (MATLAB Optimization Toolbox) was implemented in these calculations.

2.3 Calculation Results

Though each policy can theoretically produce a homogeneous copolymer in terms of its composition, the copolymer produced with each policy may have different structure and other properties. To elucidate these differences, several case studies were investigated.

Calculations were conducted based on butyl acrylate (BA)/ methyl methacrylate (MMA)/vinyl acetate (VAc) and p-methylstyrene (pMS)/MMA. The values of the kinetic and other constants, as well as the operating conditions used in the calculations, are shown in Tables 1−3. The

Table 1. Reactivity ratios used in the calculations

MMA/VAc (23)	
Monomer 1: MMA	$r_1 = 24.025$
Monomer 2: VAc	$r_2 = 0.026$
pMS/MMA 24	
Monomer 1: pMS	$r_1 = 0.419$
Monomer 2: MMA	$r_2 = 0.498$
BA/MMA (23)	
Monomer 1: BA	$r_1 = 0.298$
Monomer 2: MMA	$r_2 = 1.789$
BA/VAc (23)	
Monomer 1: BA	$r_1 = 5.939$
Monomer 2: VAc	$r_2 = 0.026$

MMA/VAc system exhibits a very large difference in reactivity ratios, $r_1/r_2 = 920$, whereas in the pMS/MMA system r_1/r_2 is 1.2. As stated before, the extent of composition drift which leads to copolymer composition heterogeneity depends on the ratio of reactivity ratios r_1/r_2, and increases with an increase in r_1/r_2. Therefore, it is much more difficult to control copolymer composition in MMA/VAc than in the pMS/MMA system.

In order to compare the different policies, not only copolymer composition characteristics, but also molecular weight averages, branching frequencies, and (selectively) sequence length and bivariate (Stockmayer bivariate molecular weight/copolymer composition) distribution characteristics were calculated. Details of the mathematical model can be found elsewhere (25).

2.4 Feed Rate

By solving Equations (1−11), monomer feed rates were calculated for each policy (Figure 2). All feed rates are different from each other. This of course leads to differences in polymer properties. As indicated before, the mole fraction of monomers in the feed stream becomes constant in policies 2 and 3, and this is confirmed in Figure 3. In the case of policy 3, the mole fraction of monomer in the feed is equal to the target copolymer composition, whereas the

mole fraction of monomer in the feed is different from the target composition in policy 2. In policy 2, when the pre-mixed monomers are used as feed, it is necessary to calculate beforehand the mole fraction of monomer in the feed needed to produce copolymer which has the desired composition. Figure 4 shows how the mole fraction of monomer in the feed stream changes with the amount of solvent used in polymerization. It is clearly shown that the feed stream composition becomes closer to the target composition with an increase in the solvent amount, as discussed above.

In policy 1, only monomer 1 (the faster monomer corresponding to the higher reactivity ratio) is fed to the reactor at a relatively slower rate compared to other policies. This might be a disadvantage for policy 1. In our calculations (for all policies), the initial volume of the reacting mixture was set to 0.6 L, typical of a lab scale reactor, and the feed rate was around 8 g/Hr (or less). So, the monomer would be fed to the reactor (in a dripping mode) as a droplet, and the concentration at the mixing (contact) point would differ from that at the other parts of the reactor (reacting mixture). Free radical polymerizations are in general rapid reactions. Therefore, if the mixing time is long compared to the reaction, heterogeneous copolymer would be produced locally. Such a situation would be more serious upon reactor scale-up.

It should also be noted that in all cases feed rates vary with time (Figure 2). This means that reliable flow control is needed in order to produce copolymer with desirable composition and maintain it at the target level.

2.5 Copolymer Composition

With the calculated feed rates in Figure 2, copolymer compositions are shown in Figure 5. From these results, it can be concluded that constant copolymer composition can be obtained with each policy. For the purpose of producing homogeneous copolymer in terms of composition, there is no difference between policies. However, polymer structure and other polymer properties would differ from each other based on different policies. This aspect will be addressed in more detail in later subsections.

Table 2. Kinetic and other constants for each monomer species (25)

|		MMA	VAc	pMS	BA
k_p	[L/mol/min]	44140.25	239251.9	15548.59	80058.48
k_t	[L/mol/min]	2.039276×10^9	5.773735×10^9	7.125829×10^9	1.250452×10^8
k_{fm}	[L/mol/min]	1.165159	3.599925	0.3711686	11.65175
k_{fp}	[L/mol/min]	0	5.742208	1.798994	35
k_{ftd}	[L/mol/min]	0	6624.231	0	0
$k_{td\%}$	[−]	0.8277016	0	0	0.7
ρ_m	[kg/L]	0.896631	0.881132	0.87102	0.85838
ρ_p	[kg/L]	1.17524	1.161974	0.87102	1.1613

p = propagation, t = termination, fm = transfer to monomer, fp = transfer to polymer, ftd = terminal double-bond polymerization, td = termination by disproportionation, td% = percentage of td in overall termination.

**Table 3.** Operating conditions for copolymerization

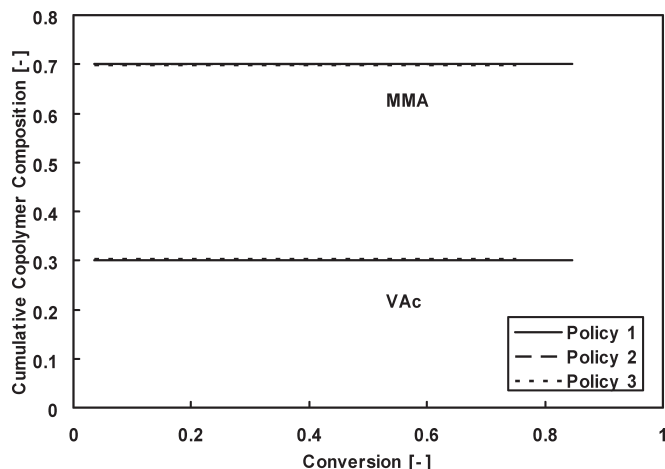|	MMA/VAc	pMS/MMA
Target composition (monomer 1/monomer 2)	0.7/0.3	0.3/0.7
N_{10} [mol]	0.159	0.3988
N_{20} [mol]	1.8653	1.3066
$[I_0]$(AIBN) [mol]	0.0426	0.0426
Toluene [L]	0.4	0.4
Temperature [°C]	60	60

Solution copolymerization with 2,2′-azo-bis-isobutyronitrile (AIBN) initiator MMA/VAc; monomer 1 = MMA, monomer 2 = VAc; pMS/MMA; monomer 1 = pMS, monomer 2 = MMA.

As stated previously, the difficulty of composition control depends on the ratio of reactivity ratios, r_1/r_2. The larger the r_1/r_2 is, the more difficult the system is to control. By 'difficulty' we mean tolerance to feed rate deviations (perturbations) from a prespecified flow rate regime. Hence, the pMS/MMA system would be more tolerant (more forgiving, less sensitive) toward such deviations than the MMA/VAc system. To illustrate this further, copolymer compositions have been calculated with a


(a)

(b)
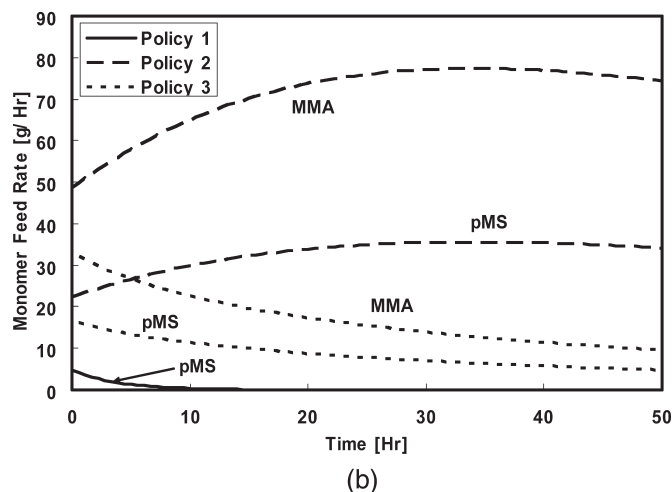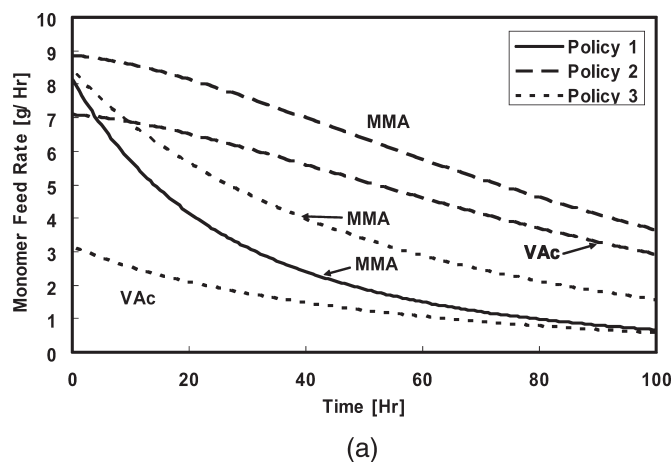
Fig. 2. Calculated feed rates, (a) MMA/VAc, (b) pMS/MMA.

(a)

(b)
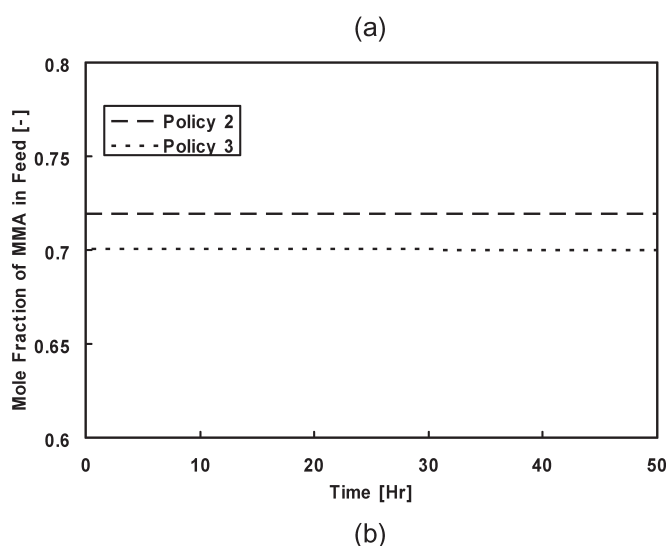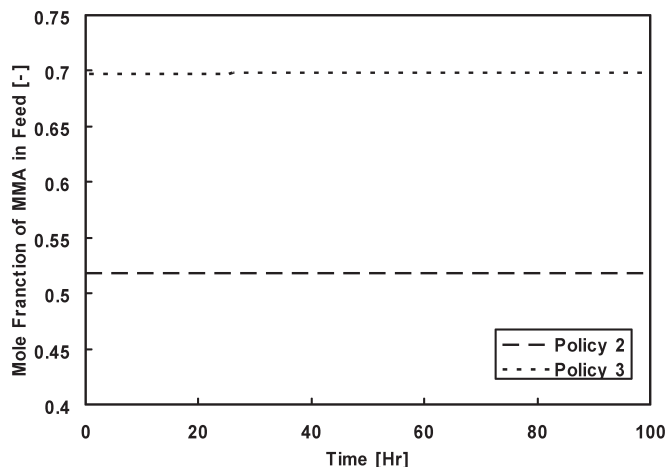
Fig. 3. Mole fraction of MMA in the feed stream, (a) MMA/VAc, (b) pMS/MMA.

'sub-optimal' constant feed rate, as shown in Figures 6 and 7. Figure 6 corresponds to the MMA/VAc case (extreme composition drift), whereas Figure 7 is for the 'milder' pMS/MMA system. In both figures, feed rates
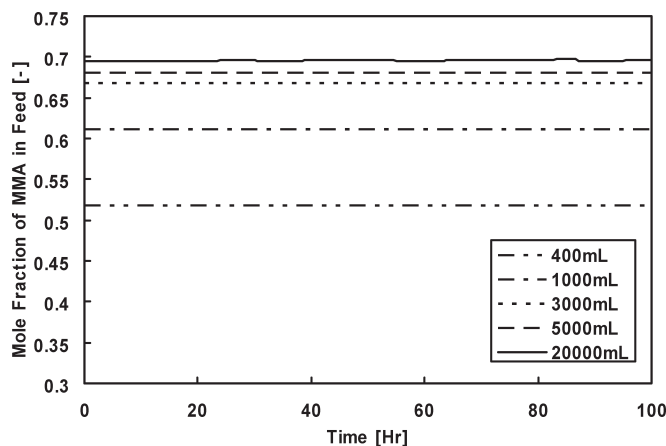
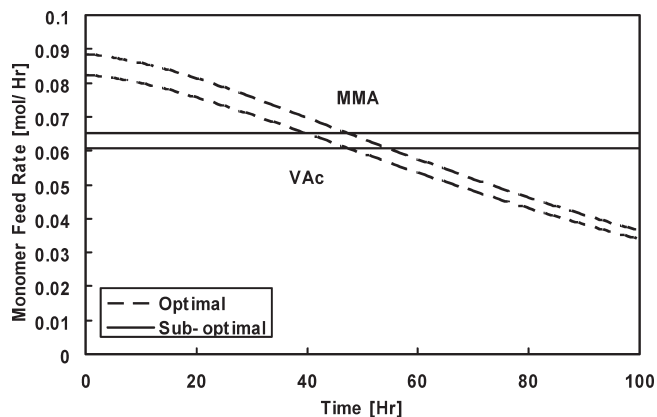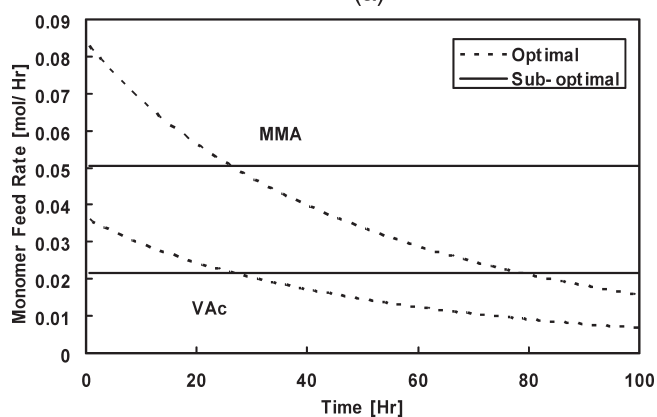**Fig. 4.** Effect of solvent amount on mole fraction of MMA in the feed in policy 2.
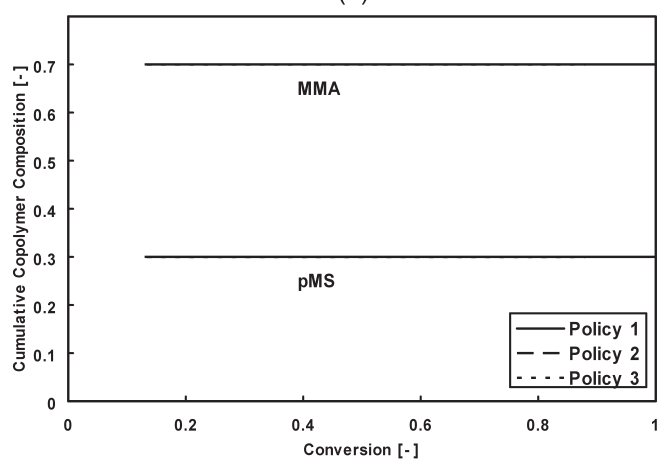
Fig. 5. Cumulative copolymer composition (based on Figure 2), a) MMA/VAc, b) pMS/MMA.

Fig. 6. Constant feed rate for MMA/VAc, a) policy 2, b) policy 3.

and calculations are shown for policies 2 and 3 (plots a and b, respectively). Figure 8 shows the corresponding cumulative copolymer compositions, calculated based on the 'sub-optimal' constant feed rates of Figures 6 and 7. The 'sub-optimal' constant rates have been arrived at by averaging the optimal feed rates (shown also in Figures 6 and 7 for comparison). The optimal feed rates (in molar flows in Figures 6 and 7, and in mass flows in Figure 2) would yield the constant target compositions of Figure 5. Instead, one obtains the situation of Figure 8. Operating with constant feed rates is much more desirable from an industrial point of view, as it simplifies pilot-plant or industrial reactor operation. There is no need for a more complicated flow control system (and pumps). As expected, almost perfect target composition was obtained in Figure 8b for the less 'difficult' pMS/MMA system. On the other hand, the behavior of Figure 8a (contrast with Figure 5a) represents deviations from the optimal policy, which (although some times tolerable, depending on the nature of the polymer product, e.g., rubber versus optical lenses) are in general unacceptable.
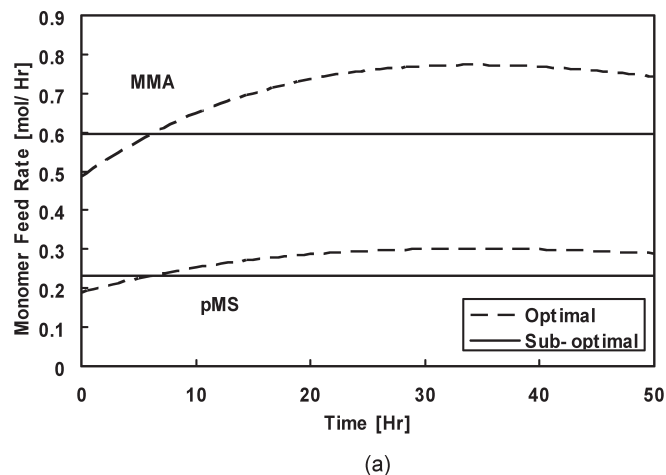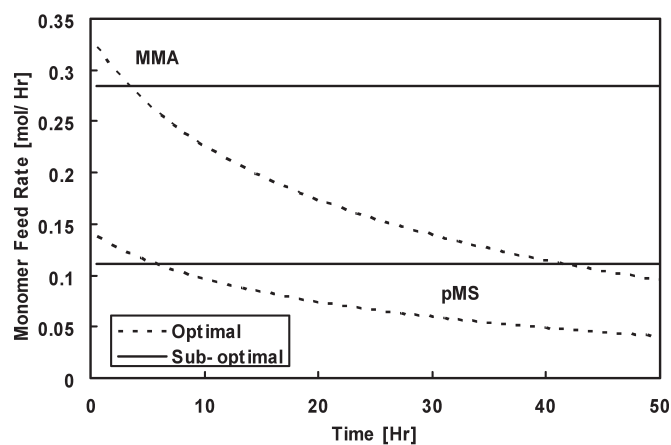
From these results, it can be concluded that tolerance toward deviations of feed rates from an optimal target depends on the ratio of the reactivity ratios, r_1/r_2. When the value of the ratio r_1/r_2 is large, more precise control is needed (at a considerably higher cost) in order to produce homogeneous copolymer.

3 Conversion

Conversion increases faster and reaches higher levels in policy 1, followed by policy 3 (intermediate between policies 1 and 2) in these solution copolymerization case studies (Figure 9). In policy 1, N_1/N_2 is kept constant and N_1 and N_2 decrease during polymerization. So, conversion tends to unity. On the other hand, the concentrations of monomers are kept constant in policy 2, so N_1 and N_2 increase during polymerization. Therefore, conversion remains at a lower value in policy 2. In policy 3, since N_1 and N_2 are kept constant, conversion becomes intermediate between policies 1 and 2. It should be noted that conversion cannot reach unity in policies 2 and 3, because in these policies unreacted monomers always exist in the reactor to some extent, hence extra monomer separation (recovery)
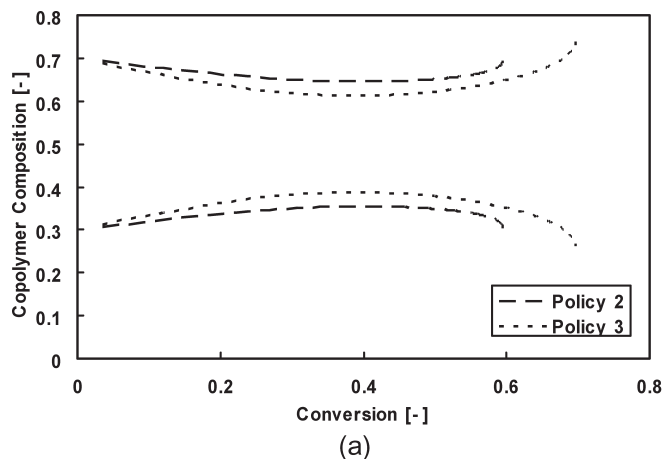
Fig. 7. Constant feed rate for pMS/MMA, a) policy 2, b) policy 3.

Fig. 8. Cumulative copolymer compositions calculated from 'sub-optimal' constant feed rate shown in Figures 6 and 7, a) MMA/VAc, b) pMS/MMA.
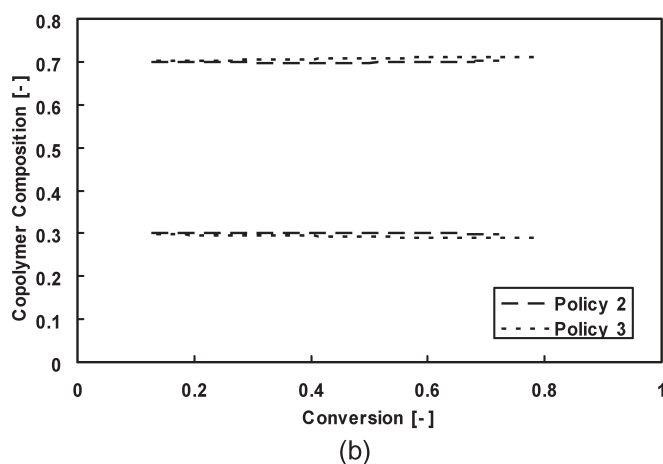
steps or batch finishing steps (3, 26) are needed. If the specifications for residual monomer are strict, policies 2 and 3 become costlier.

3.1 Molecular Weight Averages

With the feed rates of Figure 2, cumulative number-average and weight-average molecular weights were calculated (Figure 10). Policy 2 gave the largest molecular weight averages whereas policy 1 gave the lowest molecular weights (almost constant). Policy 3 was again intermediate between policies 1 and 2. This can be explained by considering the relationship between molecular weight and monomer/initiator concentration. Although in all policies initiator concentration decreases during polymerization, monomer concentration is kept constant in policy 2 (see also Figure 13, which is discussed further in the following subsection). As a result, molecular weight averages increase. On the other hand, in policy 1, monomer concentration decreases (relatively rapidly), therefore molecular weight becomes lower. In policy 3, though N_1 and N_2 are kept constant, since the volume of the reacting

mixture increases with time, monomer concentrations decrease during polymerization. However, since this change proceeds more slowly compared to policy 1, molecular weight values are larger than in policy 1 (but lower than in policy 2).

3.2 Long Chain Branching (LCB)

Figure 11 shows profiles of trifunctional long chain branching frequencies (BN3) calculated for both reference systems. BN3 is the average number of trifunctional long branches per molecule. In both systems, policy 2 exhibits the largest BN3 whereas policy 1 the smallest. Policy 3 is again intermediate between policies 1 and 2.

Trifunctional branches are mainly produced by chain transfer to polymer and terminal double bond polymerization (terminal double bonds are mainly contributed from chain transfer to monomer reactions). As shown in Figure 12, polymer concentrations are almost the same for the three policies for both systems. Therefore, it can be assumed that the contribution of terminal double bond polymerization is more or less the same for all three
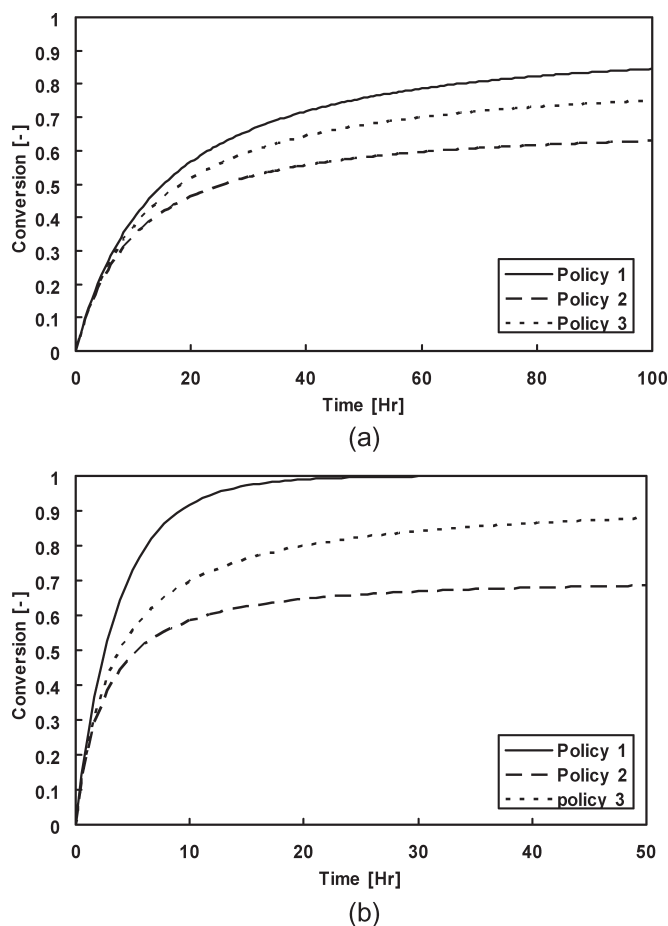
Fig. 9. Results for conversion, a) MMA/VAc, b) pMS/MMA.

Fig. 10. Results for cumulative molecular weights, a) MMA/VAc, b) pMS/MMA.

policies for both systems, and hence, what makes the difference in the BN3 profiles of Figure 11 must be the contributions from chain transfer to polymer. Since in our example the radical concentrations are more or less the same in all policies, what then causes differences in BN3 profiles from transfer to polymer is the contribution of the first moment of the dead polymer molecule population, which is related to the overall amount of monomer units consumed in the polymerization. (A number of references in the reference section cite moment equations for calculations of molecular weight/branching averages, and the reader can easily consult any one of them to see the basic equations for calculations of BN3, for instance, references (3, 4 and 25), among others). In general, policy 2 exhibits the largest first moment (compared to the other policies), since policy 2 operates under the largest monomer concentration, as shown in Figure 13. Following the same reasoning, policy 1 will have the smallest value of the first moment of the dead polymer molecule distribution, and policy 3 will be intermediate between policies 1 and 2. These trends correspond to the BN3 profiles obtained in Figure 11. Once more, as stated earlier in the general discussion about the three policies in the 'Background' section,
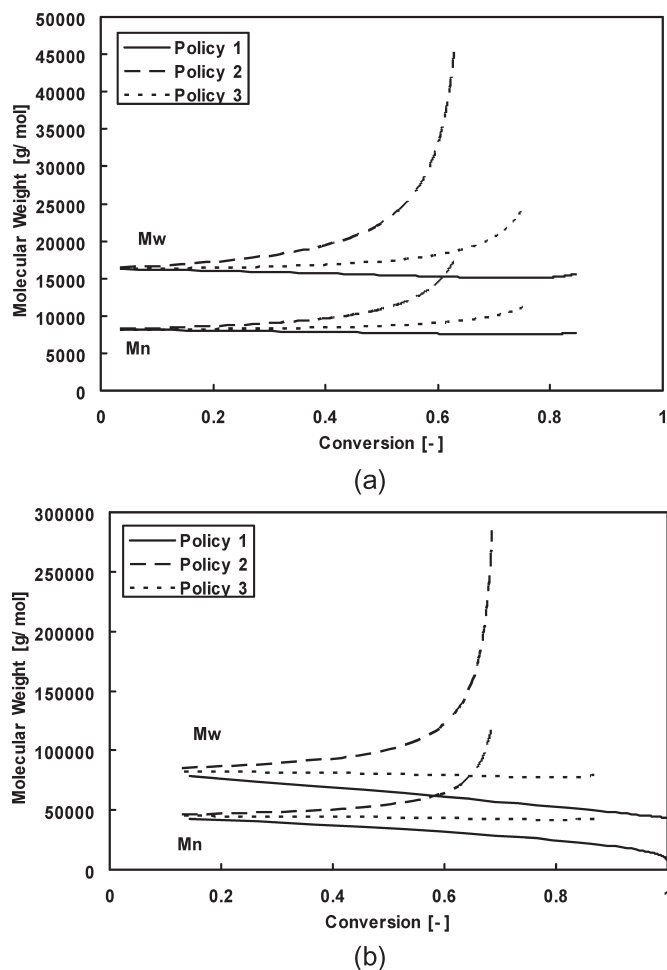
one should bear in mind that the molecular weight/branching profiles are a complicated function not only of the monomer feed policy (and hence, the rate of monomer incorporation in the copolymer chains), but also of possible combinations of the monomer feed policy with initiator/chain transfer agent/solvent flows, presence of solvent (bulk vs. solution polymerization), monomer types in the polymerizing system (and hence. their propensity towards branching reactions, e.g., VAc vs. styrene), and operating conditions (effect of temperature). In other words, the evolution of polymer properties other than copolymer composition during these semi-batch feed policies may be highly dependent on both reactor operating conditions and specific recipe. Thus, certain process factor effects (on molecular weight and branching) may be modified/moderated in the presence of solvent and/or CTA and/or combinations with initiator feed policies (or temperature programming policies). In a multi-component polymerization, these effects may be accentuated/attenuated depending on the behavior of monomers in the mixture towards branching reactions (and hence, rate of incorporation of a specific monomer in the chain).
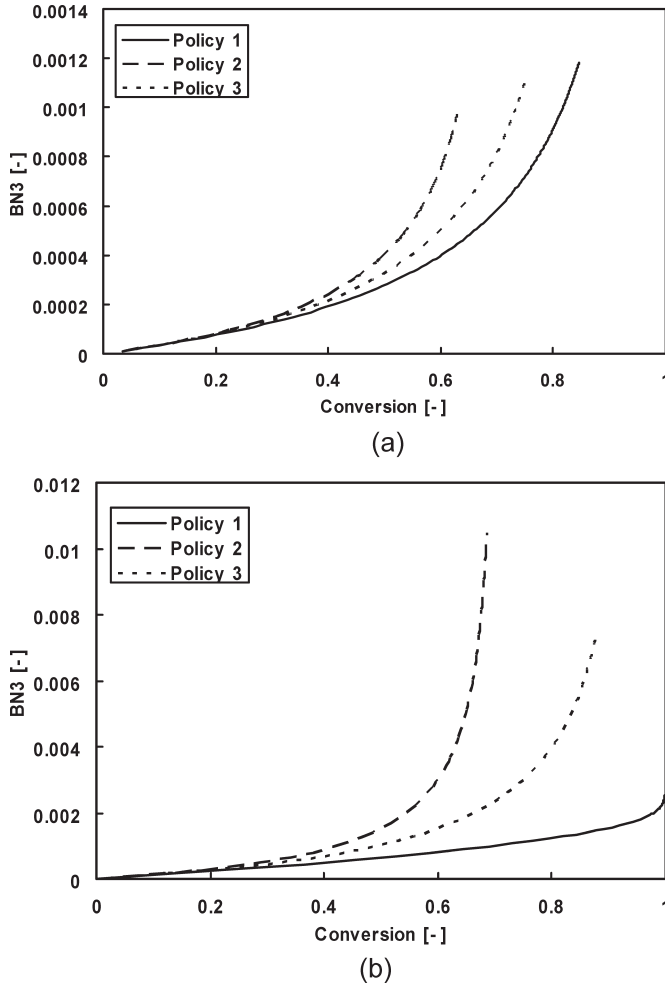
Fig. 11. Trifunctional branching frequencies, a) MMA/VAc, b) pMS/MMA.

Fig. 12. Polymer concentration.

3.3 Sequence Length Distribution

Cumulative number-average sequence length can be calculated by Equation (13) (2). (Other averages are calculated similarly and can be found elsewhere (2)).

$$(N_i)_n^{cumu} = \frac{\int_0^x F_{i,inst}(x)dx}{\int_0^x F_{i,inst}(x)dx/(N_i)_n^{inst}(x)} \tag{13}$$

$$(N_i)_n^{inst} = 1 + r_i(f_i/f_j) \tag{14}$$

where the subscripts i and j are used to designate the monomer type (i ≠ j), x is conversion, r_i denotes reactivity ratios, and $F_{i,inst}$ is instantaneous copolymer composition of monomer i.

In all policies, the same number-average sequence length is obtained. The reason for this is very obvious from Equation (14), because the monomer fraction in the reactor, f_i, is the same in all policies. It should be noted that although the two example copolymers have the same overall copolymer composition in Figure 5 (MMA/VAc = 0.7/0.3, MMA/pMS = 0.7/0.3), the cumulative number-average sequence lengths in Figure 14 differ from each other. This can be
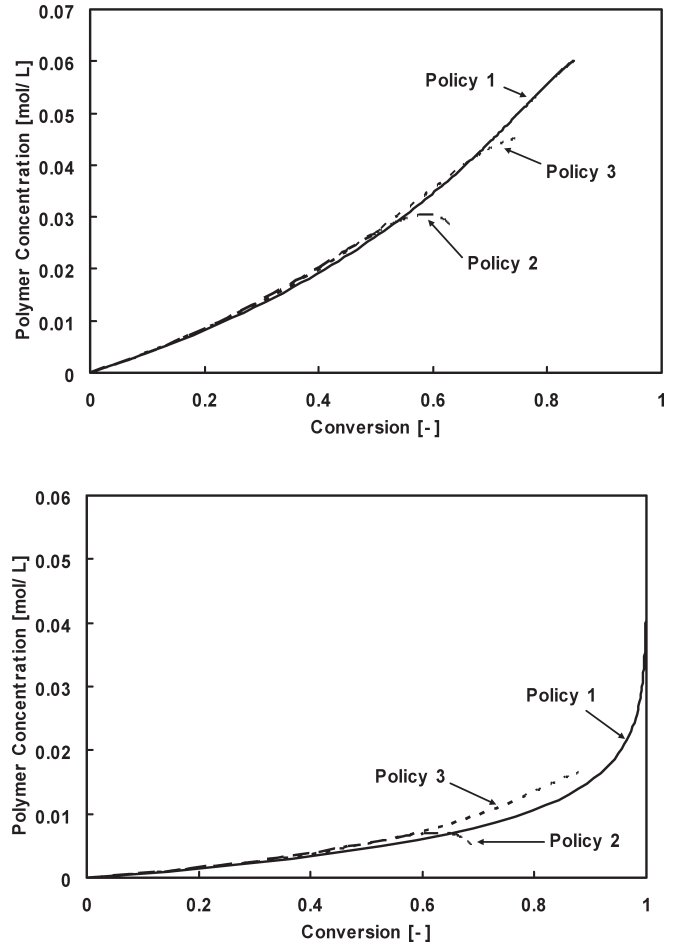
explained by the difference in reactivity ratios. In MMA/VAc, both MMA and VAc have the tendency to react with MMA, whereas in pMS/MMA MMA and pMS react with each other more randomly. Therefore, the number-average sequence length becomes smaller in the MMA/pMS system.

3.4 Triad Fractions

Cumulative triad fractions can be calculated from Equation (15) (2).

$$A_{iii}^{cumu} = \frac{1}{\int_0^x F_i(x')dx'} \int_0^x A_{iii}^{inst} F_i(x')dx' \tag{15}$$

$$A_{iii}^{inst} = \left(\frac{r_i f_i/f_j}{1 + (r_i f_i/f_j)}\right)^2 \tag{16}$$

$$A_{iij}^{inst} = \frac{r_i f_i/f_j}{(1 + (r_i f_i/f_j))^2} \tag{17}$$

$$A_{jij}^{inst} = \left(\frac{1}{1 + (r_i f_i/f_j)}\right)^2 \tag{18}$$

Fig. 13. Monomer concentrations.

Fig. 14. Cumulative number-average sequence length, a) MMA/VAc, b) pMS/MMA.
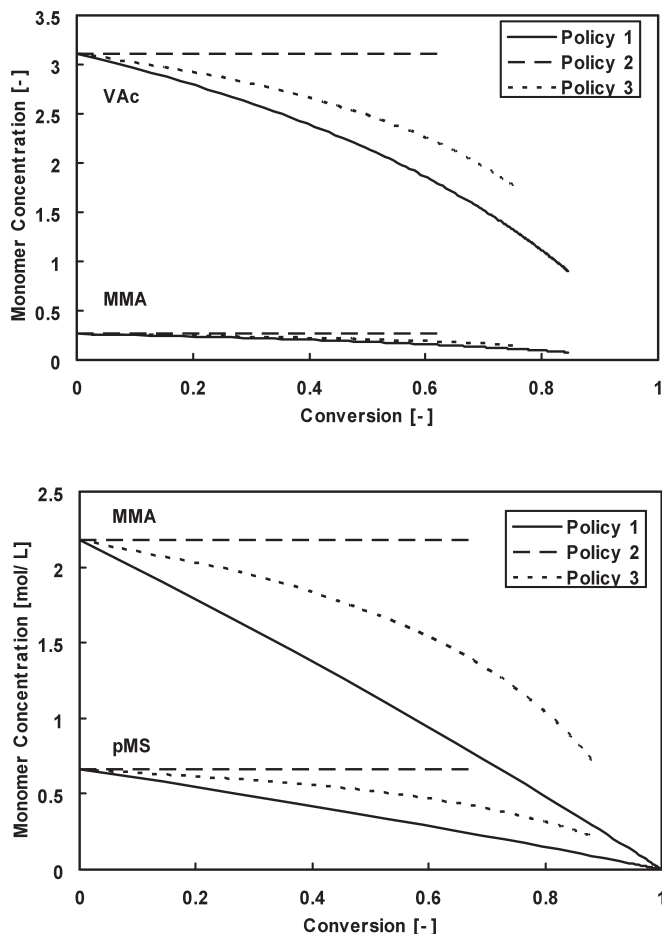
where

$$A_{iii} + A_{iij} + A_{jii} + A_{jij} = 1, \quad A_{iij} = A_{jii}$$

In all policies, the same triad fractions are obtained, because they are determined only by the monomer fraction f_i and the reactivity ratios (same in all policies).

It should be noted again that although the two copolymers have the same overall copolymer composition (MMA/VAc = 0.7/0.3. MMA/pMS = 0.7/0.3), triad fractions in Figure 15 differ from each other. This can again be explained by the differences in reactivity ratios.

3.5 Bivariate Distribution

Instantaneous bivariate (molecular weight/copolymer composition) distributions were calculated (27, 28) and are shown in Figures 16 and 17 for the two copolymer systems for different conversion levels. Strictly speaking, Equation (19) is derived for a linear copolymer. However, for relative comparison purposes between policies and since the branching levels are not significant,
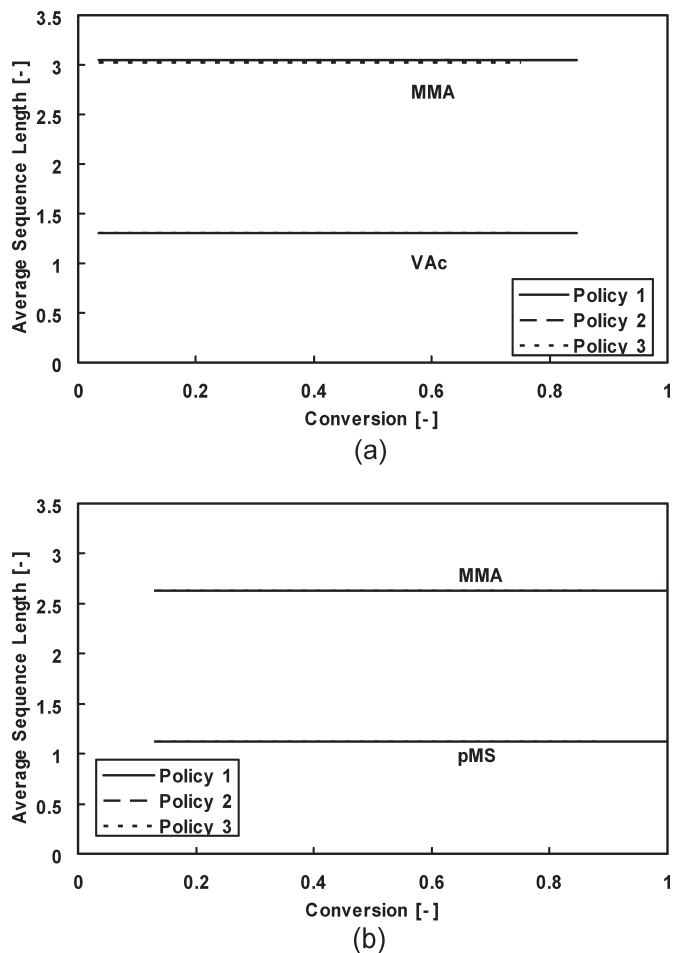
it can be assumed that Equation (19) is still valid for calculations.

$$w(r, y) = (1 + y\delta)\tau^2 r \exp(-\tau r)dr$$
$$\times \frac{1}{\sqrt{2\pi\beta/r}} \exp(-y^2 r/2\beta)dy \qquad (19)$$

where

$$\beta = \bar{F}_1(1 - \bar{F}_1)K \qquad (20)$$

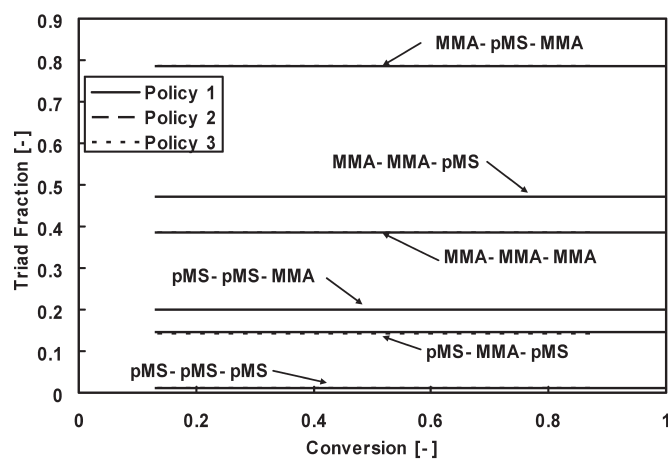$$K = [1 + 4\bar{F}_1(1 - \bar{F}_1)(r_1 r_2 - 1)]^{0.5} \qquad (21)$$

$$\delta = \frac{1 - MW_2/MW_1}{MW_2/MW_1 + \bar{F}_1(1 - MW_2/MW_1)} \qquad (22)$$

$$\tau = \frac{k_{td}[R\cdot]}{k_p[M]} + \frac{k_{fm}}{k_p} \qquad (23)$$

and $\bar{F}_1$ = average mole fraction of monomer type 1 in copolymer, y = deviation from average copolymer composition and w(r,y) = the weight fraction of copolymer of
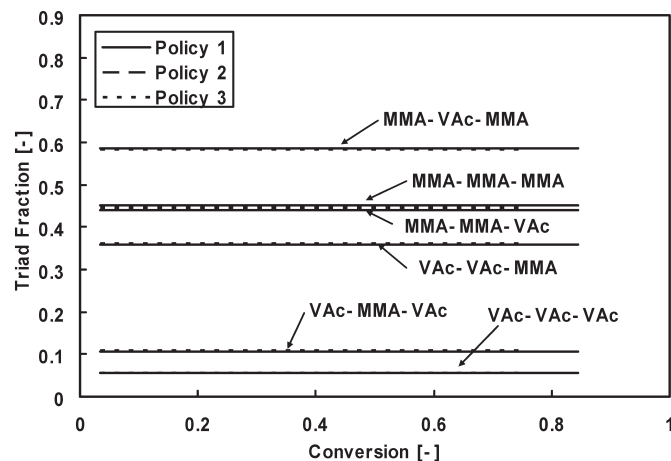
Fig. 15. Cumulative triad fractions, a) MMA/VAc, b) pMS/MMA.

Fig. 16. Results for W(y) for MMA/VAc.

chain length in the range r to r + dr and composition in the range y to y + dy for copolymer produced instantaneously (MW$_i$ denotes molecular weight of monomers 1 and 2, respectively).

From Figures 16 and 17, it can be seen that both systems show the same trends in bivariate distribution. At low conversion, there is little difference among policies, but with an increase in conversion differences among policies become more significant. W(y) is narrowest for policy 2, widest for policy 1, and intermediate (as previously) for policy 3. To explain this trend, it is necessary to consider the results for molecular weight. In general, it is known that copolymer with large molecular weight has a narrow distribution in W(y), because large molecules have composition close to the average value, which is reasonable from a statistical point of view. On the other hand, small molecule composition can easily deviate from the average, because in small molecules a difference of even a few monomer units can cause meaningful differences in composition. As discussed earlier (molecular

weight subsection and Figure 10), copolymer with larger molecular weight is produced in policy 2, whereas copolymer with relatively lower molecular weight is produced in policy 1. Therefore, W(y) exhibits the narrowest distribution in policy 2.

3.6 Extensions to Terpolymerization

The feed policies discussed above can easily be extended to terpolymer systems. In policy 1, monomers 1 and 2 are fed
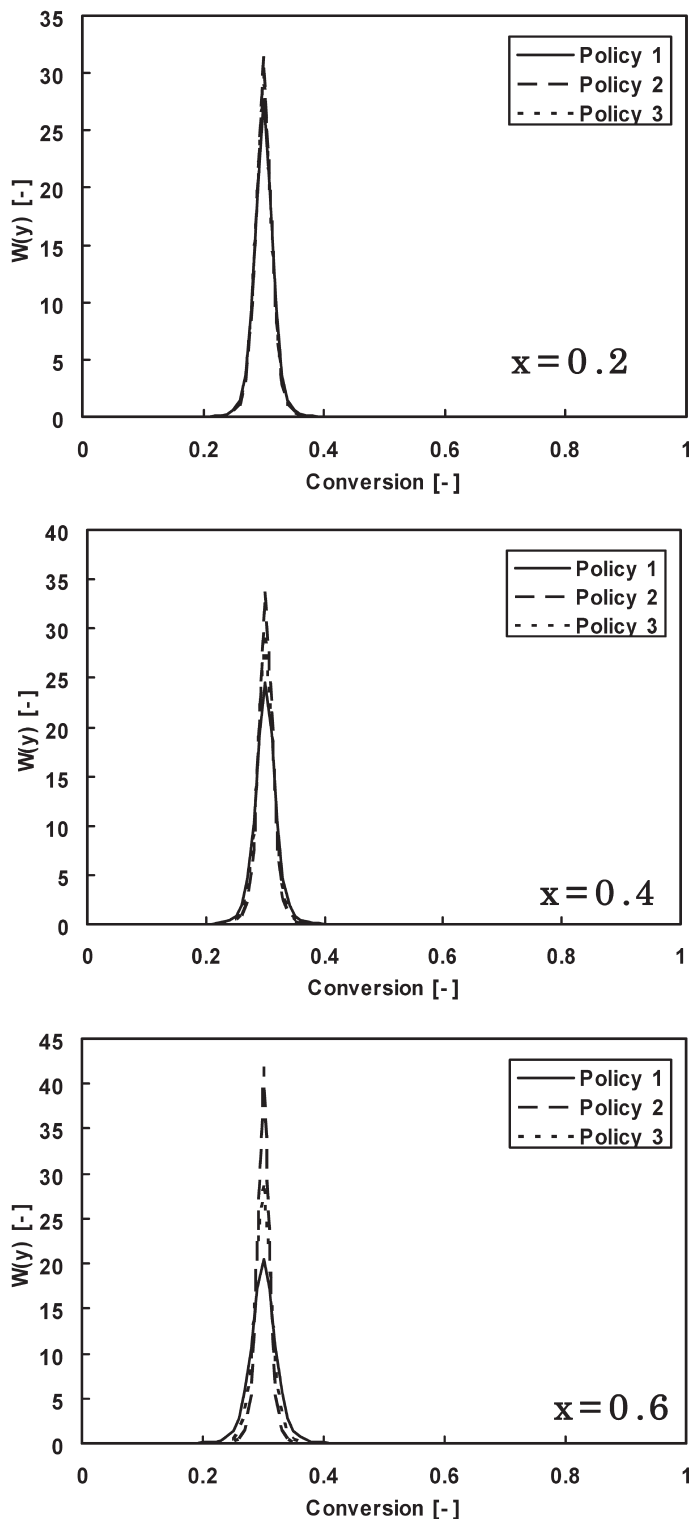
Fig. 17. Results for W(y) for pMS/MMA.

at exactly the same rate as their consumption (propagation) rate. The pertinent equations to be considered are given below.

The basic model equations are:

$$\frac{dN_1}{dt} = F_{1,in} - R_{P1}V \tag{24}$$

$$\frac{dN_2}{dt} = F_{2,in} - R_{P2}V \tag{25}$$

$$\frac{dN_3}{dt} = F_{3,in} - R_{P3}V \tag{26}$$

$$R_{P1} = -N_1(k_{11}\phi_1 + k_{21}\phi_2 + k_{31}\phi_3)[R\cdot] \tag{27}$$

$$R_{P2} = -N_2(k_{12}\phi_1 + k_{22}\phi_2 + k_{32}\phi_3)[R\cdot] \tag{28}$$

$$R_{P3} = -N_3(k_{13}\phi_1 + k_{23}\phi_2 + k_{33}\phi_3)[R\cdot] \tag{29}$$

The equation for V is as per Equation (5), whereas symbols are as defined previously for Equations (1−5). In a way analogous to Equations (6−11), the relevant conditions to be satisfied are:

Policy 1:

$$\frac{dN_1}{dt} = \left(\frac{N_1}{N_3}\right)\frac{dN_3}{dt}, \quad \frac{dN_2}{dt} = \left(\frac{N_2}{N_3}\right)\frac{dN_3}{dt} \tag{30}$$

$$F_{3,in} = 0 \tag{31}$$

Policy 2:

$$\frac{dN_1}{dt} = [M_{10}]\frac{dV}{dt} \tag{32}$$

$$\frac{dN_2}{dt} = [M_{20}]\frac{dV}{dt} \tag{33}$$

$$\frac{dN_3}{dt} = [M_{30}]\frac{dV}{dt} \tag{34}$$

Policy 3:

$$F_{1,in} = R_{P1}V \tag{35}$$

$$F_{2,in} = R_{P2}V \tag{36}$$

$$F_{3,in} = R_{P3}V \tag{37}$$

Same as in the case of copolymerization, the feed rates needed to produce homogeneous terpolymer can be calculated from the above equations. An example is shown in Figures 18 and 19 for the MMA/BA/VAc system. Initial conditions used for these calculations are shown in Table 4. From the results of Figure 19, it can be concluded that constant composition can be obtained with each policy in terpolymerization.

4 Practical Implementation

4.1 Calorimetric Control Method

As discussed earlier, each policy can provide homogeneous polymer in terms of its composition (microstructure). However, in order to calculate the required feed rates

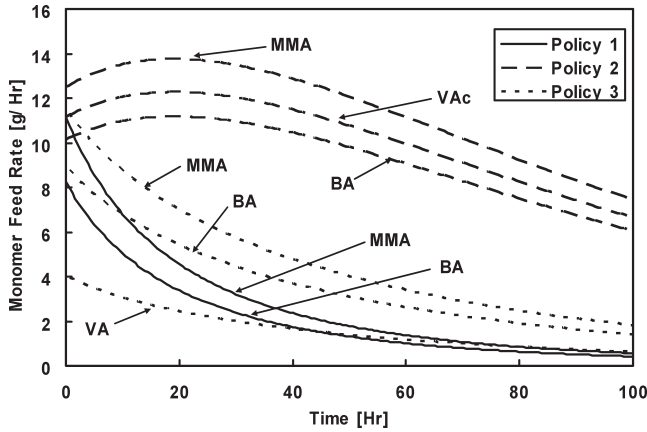to the reactor to maintain N_1/N_3 and N_2/N_3 constant. In policy 2, all three monomers are fed to the reactor at a rate maintaining M_1, M_2 and M_3 constant during polymerization. Finally, in policy 3, all three monomers are fed to the reactor

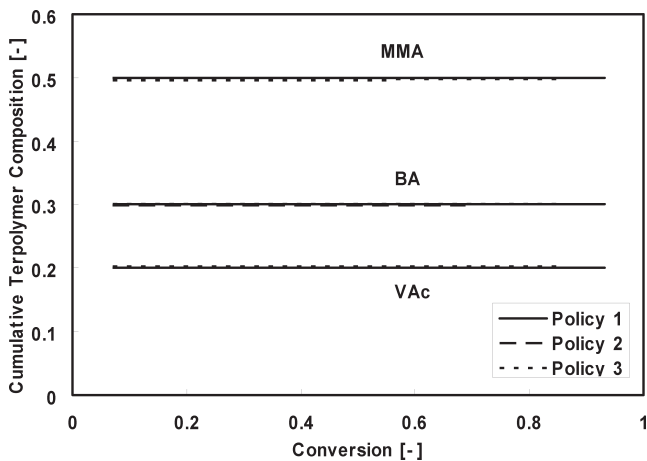**Fig. 18.** Calculated feed rates for MMA/BA/VAc.

Fig. 19. Cumulative terpolymer composition calculated based on Figure 18.

values of kinetic rate constants are needed. In addition, in order to adjust for uncontrolled variations in recipe impurities which can affect radical concentration, the use of some sort of on-line information (measurement) is required. Therefore, a calorimetric control method (being probably the most direct and straightforward of all on-line methods) was proposed

Table 4. Operating conditions for terpolymerization

	MMA/BA/VAc
Target composition (monomer 1/ monomer 2/monomer 3)	0.5/0.3/0.2
N_{10} [mol]	0.1652
N_{20} [mol]	0.1813
N_{30} [mol]	1.5811
$[I_0]$(AIBN) [mol]	0.0426
Toluene [L]	0.4
Temperature [°C]	60

Solution copolymerization with AIBN initiator.
Monomer 1 = MMA, monomer 2 = BA, monomer 3 = VAc.

(3, 4). This method will be highlighted here in more detail and will be extended in a generalized way.

The instantaneous heat generation (in energy/time) due to polymerization (VQ) is given by:

$$VQ = [(k_{11}\phi_1 + k_{21}\phi_2)N_1(-\Delta H_1) + (k_{12}\phi_1 + k_{22}\phi_2)N_2(-\Delta H_2)][R\cdot] \tag{38}$$

where V is the volume of the polymerizing mixture. Q is the instantaneous heat generation rate due to polymerization (in energy per unit volume per unit time), and $(-\Delta H)$ denotes heat of polymerization for monomers 1 and 2.

In policies 1 and 2 (policy 3 will be discussed separately later), the feed rate of monomer 1, $F_{1,in}$, is given by:

$$F_{1,in} = \frac{((k_{11} - k_{12})\phi_1 + (k_{21} - k_{22})\phi_2)N_1[R\cdot]}{(1 - \alpha N_1/N_2)} \tag{39}$$

where

$$\alpha = \frac{F_{2,in}}{F_{1,in}} \tag{40}$$

Dividing Equation (38) by Equation (39), and thus eliminating the total polymer radical concentration, one obtains:

$$\frac{VQ}{F_{1,in}} = \frac{\begin{array}{c}(k_{11}\phi_1 + k_{21}\phi_2)(-\Delta H_1)\\ +(k_{12}\phi_1 + k_{22}\phi_2)(-\Delta H_2)(N_2/N_1)\end{array}}{(k_{11} - k_{12})\phi_1 + (k_{21} - k_{22})\phi_2/1 - \alpha(N_1/N_2)} \tag{41}$$

If the two monomers are premixed and fed to the reactor in one stream, α is a constant. (Actually, in policy 2, α is kept constant during polymerization as one can easily see from the definition of α and the results of Figure 3) It should be recalled that ϕ_1 and ϕ_2 are both functions of N_1/N_2 and polymerization temperature. The temperature dependence of ϕ_i should be small because the activation energies of the cross-propagation constants are similar in magnitude. In fact, the right-hand side of Equation (41) should have a weak temperature dependence. In other words, to maintain constant composition F_1 for the copolymer being produced, one should control the monomer feed rate to maintain $VQ/F_{1,in}$ constant with time.

As discussed above, in policy 2, α is kept constant during polymerization (needless to say, in policy 1, $\alpha = 0$ during polymerization). Therefore, the calorimetric control method can be applied to both policies 1 and 2. This can easily be confirmed. Monomer feed rates can be calculated to follow:

$$F_{1,in} = \frac{VQ}{(VQ_0/F_{1,in0})} \tag{42}$$

$$F_{2,in} = \alpha_0 F_{1,in} \quad (\alpha_0 = F_{2,in0}/F_{1,in0}) \tag{43}$$

$F_{1,in0}$ and $F_{2,in0}$ can be calculated using a trial-and-error method.

An example of this calculation is shown in Figure 20. From this figure, it is obvious that the calorimetric control method can yield copolymers with constant composition for both policies (see also Figure 5).
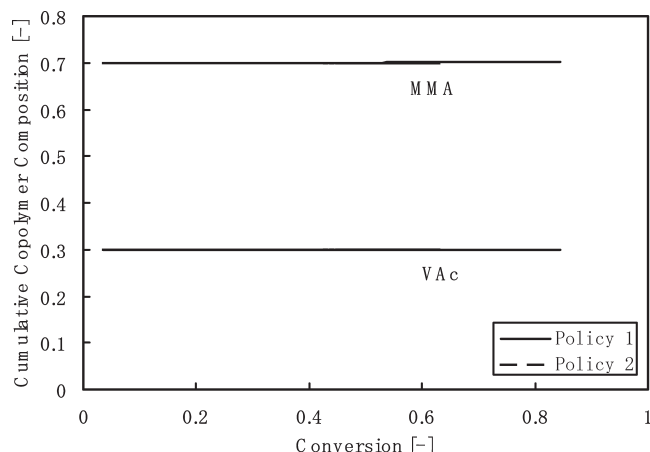
Fig. 20. Cumulative copolymer composition with $VQ/F_{1,in} =$ const for MMA/VAc.

The most prominent feature of this method is that we do not need to know exact values of kinetic rate constants, which are not always available or accurate. VQ data will give direct information about propagation rate, and it is the propagation rate that we need to know to calculate the monomer feed rates, not the rate constants.

The practical implementation of the calorimetric control method is quite simple. Once the target copolymer composition, F_1, is specified, the monomer ratio N_1/N_2 to be kept constant during polymerization can be calculated using reactivity ratios. Then we just need to operate the semi-batch process so as to keep $VQ/F_{1,in}$ constant. However, there are still parameters to be known, namely, reactivity ratios and the value of $VQ/F_{1,in}$. Regarding reactivity ratios, extensive literature is available and they can be estimated with sufficient accuracy (29). So, the issue is how to determine the value of $VQ/F_{1,in}$. Three methods of determining $VQ/F_{1,in}$ are proposed here.

(1) $VQ/F_{1,in}$ can be determined experimentally. $VQ/F_{1,in}$ can be expressed in the form:

$$\frac{VQ}{F_{1,in}} = \frac{VQ}{R_{P1}V - R_{P2}VN_1/N_2/(1 - \alpha(N_1/N_2))} \quad (44)$$

VQ is measured during polymerization (energy balance). Estimates of $R_{p1}V$ and $R_{p2}V$ can be obtained from batch reactor experiments. For example, from a low conversion batch experiment, monomer concentration data can be obtained, and $R_{p1}V$ and $R_{p2}V$ can subsequently be calculated from the slope of monomer concentration vs. time curve.

(2) N_2/N_1 can be thought of as a function of $VQ/F_{1,in}$ (see Equation (45) based on Equation (41)). Therefore, the estimation of $VQ/F_{1,in}$ becomes an optimization problem by solving a nonlinear equation. In practice, $VQ/F_{1,in}$ can be obtained by an iterative procedure during polymerization. The value of N_2/N_1 can be measured, for example, by gas/liquid chromatography, and $VQ/F_{1,in}$ can be adjusted

accordingly based on the required functional dependence of N_2/N_1 vs. $VQ/F_{1,in}$ established beforehand.

$$\frac{N_2}{N_1} = g\left(\frac{VQ}{F_{1,in}}\right) \quad (45)$$

(3) After some algebra and starting with Equation (41), $VQ/F_{1,in}$ can also be given by Equation (46). In this equation, the unknown entities are $(-\Delta H_1)$ and $(-\Delta H_2)$. If $(-\Delta H_1)$ and $(-\Delta H_2)$ can be estimated experimentally, $VQ/F_{1,in}$ can be calculated directly.

$$\frac{VQ}{F_{1,in}} = \frac{(r_1 + c)(-\Delta H_1) + (1 + r_2 c)(-\Delta H_2)c}{(r_1 - 1) + (1 - r_2)c/(1 - a/c)} \quad (46)$$

where

$$c = \frac{N_2}{N_1} \quad (47)$$

and r_1 and r_2 are reactivity ratios.

The calorimetric control method can also be extended to policy 3. In policy 3, monomers should be fed to the reactor at a rate equal to their consumption rate, hence $F_{1,in} + F_{2,in}$ must be equal to the overall propagation rate. Hence, by taking the ratio of VQ to $F_{1,in} + F_{2,in}$, a simple relationship can be obtained:

$$\frac{VQ}{F_{1,in} + F_{2,in}} = \frac{R_{P1}(-\Delta H_1) + R_{P2}(-\Delta H_2)}{R_{p1} + R_{P2}}$$

$$= F_1(-\Delta H_1) + F_2(-\Delta H_2) \quad (48)$$

Obviously, the right-hand side of Equation (48) is kept constant during polymerization. In order to produce homogeneous copolymer, monomers need to be fed into the reactor according to Equation (49).

$$F_{1,in} + F_{2,in} = \frac{VQ}{F_1(-\Delta H_1) + F_2(-\Delta H_2)} \quad (49)$$

Sample calculations are shown in Figures 21 and 22. From these results, it is concluded that the calorimetric control
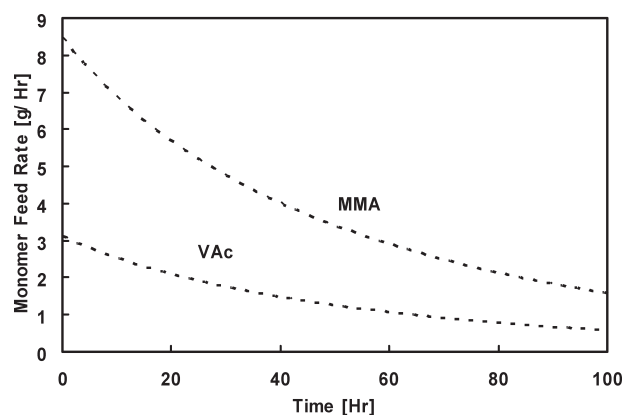

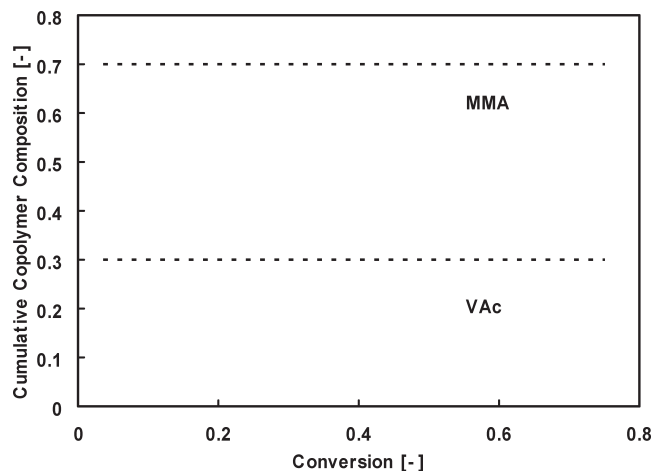**Fig. 21.** Calculated feed rates with $VQ/(F_{1,in} + F_{2,in}) =$ const in policy 3 for MMA/VAc.

Fig. 22. Cumulative copolymer composition calculated from Figure 21.

Fig. 23. Cumulative copolymer composition for starved solution polymerization.

method is also valid in policy 3. The results can be directly compared with Figures 2 and 5.

4.2 Starved Polymerization

The most straightforward way to produce homogeneous copolymer is carrying out the polymerization under starved conditions, hence the popularity of this technique over the years. In emulsion polymerization, this technique has been widely and successfully implemented (30, 31). In this way, the polymerization becomes controlled by the addition rate of monomers and the reaction rate of both monomers (hence, the monomer unit insertion rate) is the same as the feed rate. This results in a copolymer of the same composition as the feed. Namely, all we have to do is just prepare a monomer solution which has the same composition as the target copolymer composition and feed it slowly enough into the reactor. In this case, a priori calculation of the initial monomer feed composition is not needed, as with the other policies. Hence, we do not need to have a priori estimates of reactivity ratios.

However, this is not the case in solution polymerization. Feeding slowly the monomer mixture (which has the same composition as the target copolymer) does not produce a homogeneous copolymer in solution polymerization, as shown in Figure 23. In this sample calculation, a monomer mixture with molar composition, MMA:VAc = 7:3, is fed to the reactor (MMA = monomer 1). The reactor contains only the appropriate amounts of solvent and initiator. Monomers are subsequently fed in order to keep the feed rate slower than the propagation rate, namely, at $F_{2,in} = R_{P2}V$ and $F_{1,in} = 7/3F_{2,in}$. It is obvious from the results of Figure 23 that copolymer composition drifts during polymerization, especially at the later stages of conversion.

When arbitrarily 'dripping in' the monomer feed, as it usually happens in typical implementations of the starved technique, at the moment a monomer droplet reaches the reaction mixture at t = 0, the mole fraction of monomer 1
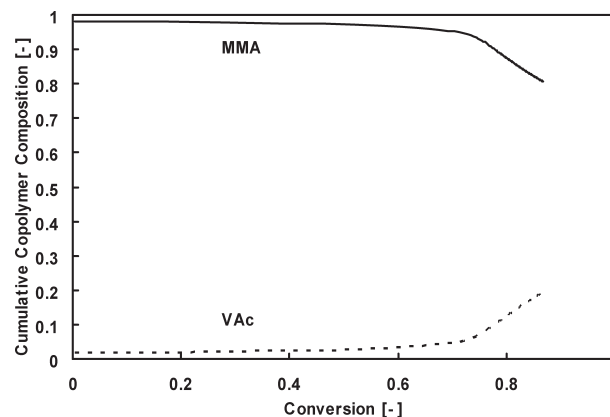
in the reactor is equal to 0.7. The composition of the corresponding copolymer produced at this moment is determined according to the Mayo-Lewis equation. In this case, the instantaneous copolymer composition becomes 0.98. When the next monomer droplet comes into the mixture, monomer concentrations in the reactor are very low, but not necessarily equal to zero. Thus, the mole fraction of monomer is slightly different from that at the previous instant. In this way, composition drift will occur.

If the initial monomer feed has the appropriate composition calculated from the Mayo-Lewis equation, then homogeneous copolymer will be produced, as the starved operation becomes the same as policy 3.

In summary, if we run an emulsion polymerization under starved conditions, a priori knowledge of reactivity ratios is not needed. However, for solution polymerization, one needs to know these reactivity ratios (hence, run some experiments beforehand in order to estimate r_1 and r_2) since one has to be able to calculate the initial monomer feed composition needed to give the desired copolymer composition.

5 Gradient Block Copolymers

Gradient copolymers, an interesting class of materials, have been the subject of recent investigations (5, 6). A gradient copolymer is defined as a copolymer where the monomer composition changes continuously along the backbone from predominantly A to predominantly B (32). The composition of an A-B gradient copolymer is best described as being between two extremes, namely between the corresponding diblock copolymer and a random copolymer, and thus it has been predicted that thermal and other properties of a gradient copolymer should deviate from those of random or diblock copolymers (7).

There are several ways of making gradient copolymer. In gradient copolymer, the instantaneous composition of the polymer must change continuously along the chain. For this, all kinds of polymerizations without the termination

step can be applied (for instance, controlled radical and living polymerization techniques).

Two approaches are available to produce gradient copolymer. First, gradient copolymer can be produced spontaneously in a batch reactor because of different monomer reactivities. However, in this way, complete homo-grad(ient)-homo structure can not be obtained; what is obtained is rather something intermediate between diblock and random. In order to produce a complete homo-grad-homo structure, it is necessary to use a semi-batch process, with the following steps:

Step 1: homopolymerization of monomer A block in batch
Step 2: copolymerization and formation of gradient block in semi-batch
Step 3: homopolymerization of monomer B block in batch (or semi-batch)

The copolymer gradient itself is the derivative of instantaneous copolymer composition with respect to chain length and it is this gradient that may have great impact on how polymer properties vary. Using semi-batch feed allows us to control the gradient, and therefore, it is possible to control polymer microstructure and properties. Therefore, finding an appropriate feed rate becomes of great interest.

Though many kinds of gradient are possible, recently 'linear gradient' (otherwise referred to as 'compositionally constant gradient') copolymers have been studied intensively and in some special cases, analytical solutions have been attempted (33). The main focus here is to outline a numerical procedure in order to calculate the required feed rate in a generalized manner.

Since in order to produce gradient copolymers polymerizations must be conducted without the termination step, the molar balances for the model equations are modified as follows:

$$\frac{dN_1}{dt} = -(k_{11}\phi_1 + k_{21}\phi_2)[I_0]N_1 + F_{1,in} \qquad (50)$$

$$\frac{dN_2}{dt} = -(k_{12}\phi_1 + k_{22}\phi_2)[I_0]N_2 + F_{2,in} \qquad (51)$$

$$\frac{dP_1}{dt} = (k_{11}\phi_1 + k_{21}\phi_2)[I_0]N_1 \qquad (52)$$

$$\frac{dP_2}{dt} = (k_{12}\phi_1 + k_{22}\phi_2)[I_0]N_2 \qquad (53)$$

Symbols in Equations (50–53) are as before, with the new additions of P_1 and P_2 depicting moles of monomer 1 and 2 bound as polymer, and $[I_0]$ representing concentration of initiator.

The copolymer composition gradient is defined (34) as the derivative of instantaneous copolymer composition, $F_{1,inst}$, with respect to chain length (as shown in Figure 24). In the case of a 'linear gradient' copolymer, the derivative becomes constant and equal to Φ. The composition changes linearly from $F_{1,inst} = 1.0$ to $F_{1,inst} = 0.0$ along the chain, and Φ becomes equal to $-1/Xe$, where Xe is the chain length of the gradient block. Since it is more tedious to
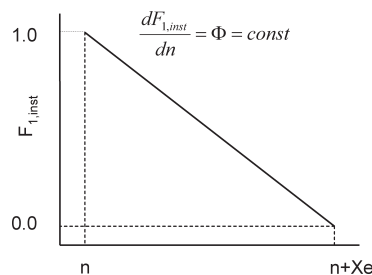

Fig. 24. Definition of gradient (instantaneous composition vs. chain length).

calculate $dF_{1,inst}/dn$, where n denotes chain length, the integrated form, Equation (54), is used in the calculations:

$$F_{1,inst} = 1 + \Phi n \qquad (54)$$

Chain length n can be calculated from Equation (55):

$$n = \frac{P_1 + P_2}{[I_0]} \qquad (55)$$

In order to calculate monomer feed rates, one more condition is needed. Though there are many possibilities for this condition, for the sake of simplicity the condition adopted here is:

$$F_{1,in} = 0 \qquad (56)$$

Now there are enough equations in order to calculate monomer feed rates. Other conditions can be used for this calculation. For example, keeping the total propagation rate constant during polymerization can be used as a condition for feed rate calculations (33). With any condition, the basic procedure to calculate the feed rate is similar to that described herein. However, there is still one unresolved issue, namely $F_{1,inst}$. In order to calculate monomer feed rate, it is necessary to define $F_{1,inst}$ concretely. In the case of conventional free radical polymerization, the definition of instantaneous
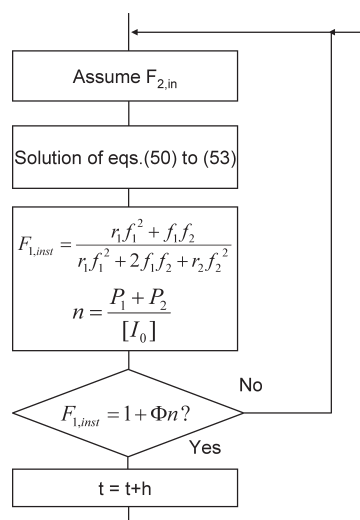

Fig. 25. Procedure to calculate feed rate to produce desired gradient copolymer.
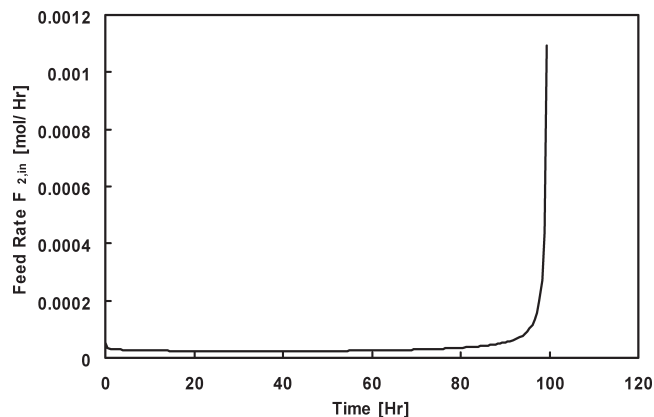
Fig. 26. Feed rate needed to produce desired gradient.

copolymer is more obvious, and therefore instantaneous composition is the composition of copolymer produced during an infinitesimal time period, given by the Mayo-Lewis equation:

$$F_{1,inst} = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \qquad (57)$$

However, in the case of living polymerization the same definition might not be applied, because in living polymerization all chains are growing gradually. Hence, the instantaneous composition should be defined as the composition of a part of the polymer chain produced during a specific time period. However, for this analysis, we will assume that the Mayo-Lewis equation is still valid. The Mayo-Lewis equation is derived from the ratio of the consumption rate of each monomer to the overall monomer consumption rate, and, whether the polymerization is living or conventional radical, the instantaneous composition is determined by the ratio of these consumption rates. Therefore, the Mayo-Lewis equation was used to calculate $F_{1,inst}$ in the simulations of this section. Checking the validity of the Mayo-Lewis equation will be discussed shortly.
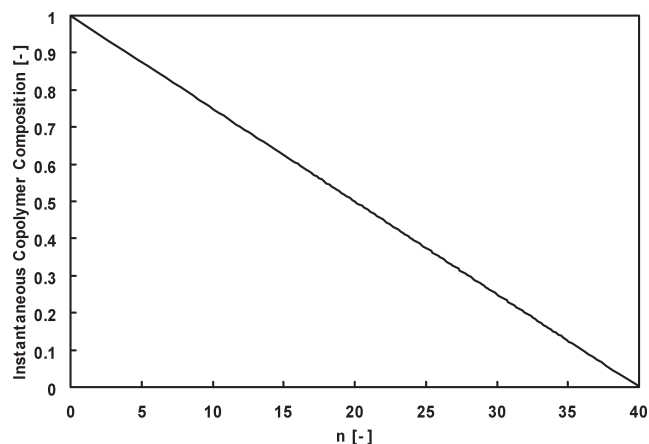
Table 5. Parameters for gradient copolymer

k_{11} [L/mol/min]	8.228
k_{22} [L/mol/min]	47.85
k_{12} [L/mol/min]	0.3424
k_{21} [L/mol/min]	1832.8
N_{10} [mol]	0.003928
N_{20} [mol]	0
$[I_0]$ [mol]	0.000159
Φ [$-$]	-0.025

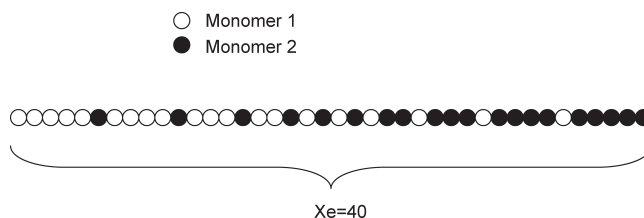Hypothetical monomer system; solution polymerization.

Fig. 28. Actual gradient block with chain length = 40.

The model equations are solved numerically according to the procedure of Figure 25. Sample calculations are shown in Figures 26 and 27. The values of all parameters used in the calculations are shown in Table 5. The monomer 2 feed rate is shown in Figure 26, and with this feed rate, the instantaneous composition changes linearly (Figure 27).

As discussed above, the Mayo-Lewis equation was used in this demonstration, hence, it is instructive to say a few words about checking the validity of using the Mayo-Lewis equation in this case study. For this purpose, a comparison was conducted between the calculated cumulative copolymer composition and the actual gradient block composition. In the calculation result shown in Figure 27, the chain length of the gradient block is 40, whereas the actual gradient block composed of 40 monomer units is depicted in Figure 28. From Figure 28, the cumulative copolymer composition of
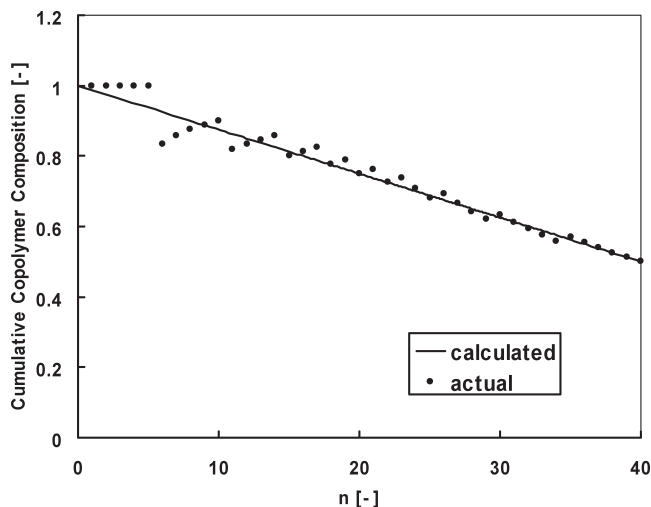

Fig. 27. Instantaneous copolymer composition vs. chain length based on Figure 26.

Fig. 29. Cumulative copolymer composition change along the chain.

the actual gradient block can be directly determined. The comparison of the results is shown in Figure 29. Some discrepancy can be seen for small chain lengths (n less than 15), which is inevitable because in the actual chain the composition changes discontinuously. However, when the chain length becomes larger (n > 15), the discrepancy becomes smaller and eventually good agreement can be seen. Therefore, from this result, it is concluded that the Mayo-Lewis equation is valid as long as the chain length is sufficiently large (for all practical purposes, larger than 10–15 units).

6 Concluding Remarks

Characteristic features of three classes of copolymer composition control policies and their modifications were investigated, with applications on typical copolymer systems. Generalized extensions to multicomponent systems and practical implementation were also derived and discussed. There is no such thing as the 'best' policy. The optimality of the policy depends eventually on the effects of the operational policy on a range of polymer properties, which will have significant impact on specific polymer product uses. These effects are dependent on operating conditions and are recipe- and monomer mixture case-specific. Several pros and cons of these policies were highlighted.

Traditionally, laboratory research and polymer product screening are conducted with batch type reactors. Only a narrow segment of the multidimensional polymer property distributions and polymer microstructure can be highlighted with batch reactors. In order to capture more of the multitude of possibilities of polymer microstructure with a minimum of screening experiments, semi-batch (semi-continuous) reactor operating modes and related (statistical) experimental designs should be pursued for more effective new copolymer product design and evaluation.

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8 References

1. Odian, G. *Principles of Polymerization*, 4th edn; John Wiley & Sons: New York, 2004.
2. Dotson, N., Galvan, R., Laurence, R. and Tirrell, M. *Polymerization Process Modeling*; John Wiley & Sons: New York, 1996.
3. Hamielec, A.E., MacGregor, J.F. and Penlidis, A. (1987) *Makromol. Chem. Macromol. Symp.*, **10/11**, 521–570.
4. Dubé, M.A., Soares, J.B.P., Penlidis, A. and Hamielec, A.E. (1997) *Ind. Eng. Chem. Res.*, **36**, 966–1015.
5. Greszta, D. and Matyjaszewski, K. (1996) *Polym. Prepr.*, **37(1)**, 569–570.
6. Arehart, S.V., Greszta, D. and Matyjaszewski, K. (1997) *Polym. Prepr.*, **38(1)**, 705–706.
7. Pakula, T. (1996) *Macromol. Theory Simul.*, **5(5)**, 987–1006.
8. Johnson, A.F., Khaligh, B. and Ramsay, J. (1982) ACS Symposium Series **197**, 117–135.
9. Arzamendi, G. and Asua, J.M. (1989) *J. Appl. Polym. Sci.*, **38**, 2019–2036.
10. Arzamendi, G. and Asua, J.M. (1990) *Makromol. Chem., Macromol. Symp.*, **35/36**, 249–268.
11. Arzamendi, G. and Asua, J.M. (1991) *Ind. Eng. Chem. Res.*, **30**, 1342–1350.
12. Arzamendi, G., Leiza, J. and Asua, J.M. (1991) *J. Polym. Sci., Part A: Polym. Chem.*, **29**, 1549–1559.
13. Arzamendi, G., de la Cal, J.C. and Asua, J.M. (1992) *Angew. Makromol. Chem.*, **197**, 47–64.
14. van Doremaele, G.H., Schoonbrood, H.A.S., Kurja, J. and German, A.L. (1992) *J. Appl. Polym. Sci.*, **45**, 957–966.
15. Leiza, J.R., Azramendi, G. and Asua, J.M. (1993) *Polym. Int.*, **30**, 455–460.
16. Schoonbrood, H.A.S., Thijssen, H.A., Brouns, H.M.G., Peters, M. and German, A.L. (1993) *J. Appl. Polym. Sci.*, **49**, 2029–2040.
17. Schoonbrood, H.A.S., van Eijnatten, R.C.P.M. and German, A.L. (1996) *J. Polym. Sci., Polym. Chem.*, **34**, 949–955.
18. Canegallo, S., Canu, P., Morbidelli, M. and Storti, G. (1994) *J. Appl. Polym. Sci.*, **54**, 1919–1935.
19. Canu, P., Canegallo, S., Morbidelli, M. and Storti, G. (1994) *J. Appl. Polym. Sci.*, **54**, 1899–1917.
20. Urretabizkaia, A., Arzamendi, G., Unzue, M.J. and Asua, J.M. (1994) *J. Polym. Sci., Polym. Chem.*, **32**, 1779–1788.
21. de la Cal, J.C., Echevarria, A., Meira, G.R. and Asua, J.M. (1995) *J. Appl. Polym. Sci.*, **57**, 1063–1074.
22. Echevarria, A., de la Cal, J.C. and Asua, J.M. (1995) *J. Appl. Polym. Sci.*, **57**, 1217–1226.
23. (a) Dubé, M.A. and Penlidis, A. *Polymer*, 1995, **36**, 587–598; (b) Dubé, M.A. and Penlidis, A. (1997) *J. Polym. Sci., Polym. Chem.*, **35**, 1659–1672; (c) Dubé, M.A. and Penlidis, A. (1995) *Macromol. Chem. Phys.*, **196**, 1101–1112.
24. Jones, K.M., Bhattacharya, D., Brash, J.L. and Hamielec, A.E. (1986) *Polymer*, **27**, 602–610.
25. WATPOLY Database Simulation package, as in; (a) Gao, J. and Penlidis, A. *J. Macromol. Sci., Revs. Macromol. Chem. Phys.*, 1996, **C36**, 199–404; (b) Gao, J. and Penlidis, A. (1998) *J. Macromol. Sci., Revs. Macromol. Chem. Phys.*, **C38**, 651–780.
26. O'Driscoll, K.F., Ponnuswamy, S.R. and Penlidis, A. (1989) ACS Symposium Series **404**, 321–336.
27. Stockmayer, W.H. (1945) *J. Chem. Phys.*, **13**, 199–207.
28. Tacx, J.C.J.F., Linssen, H.N. and German, A.L. (1988) *J. Polym. Sci., Polym. Chem.*, **26**, 61–69.
29. Polic, A.L., Duever, T.A. and Penlidis, A. (1998) *J. Polym. Sci., Polym. Chem.*, **36**, 813–822.
30. Snuparek, J. and Krska, F. (1977) *J. Appl. Polym. Sci.*, **21**, 2253–2260.
31. El-Aasser, M.S., Makgewinata, T., Vanderhoff, J.W. and Pichot, C. (1983) *J. Polym. Sci., Polym. Chem.*, **21**, 2363–2382.
32. Dettmer, C.M., Gray, M.K., Torkelson, J.M. and Nguyen, S.T. (2004) *Macromolecules*, **37**, 5504–5512.
33. Beginn, U. (2006) *Polymer*, **47**, 6880–6894.
34. Mignard, E., Leblanc, T., Bertin, D., Guerret, O. and Reed, W.F. (2004) *Macromolecules*, **37**, 966–975.