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High Temperature Semibatch Free Radical Copolymerization of Dodecyl Methacrylate and Styrene

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Summary: High temperature semibatch free radical copolymerizations of dodecyl methacrylate (DMA) and styrene (ST) were carried out. A mechanistic model including depropagation and penultimate chain growth was built in Predici®. The comparison between the simulated and the experimental final polymer molecular weights indicates that the initiator efficiency decreases when DMA is used as a comonomer. Using estimated initiator efficiencies and termination coefficients, the model provides good fits to the complete set of experimental data.

Keywords: copolymerization; dodecyl methacrylate; kinetics (polym.); modeling; styrene

Introduction

Copolymers of methacrylate and styrene are the main components in many automotive coating formulations because of their excellent chemical properties. Driven by legislative pressures to reduce environmental emissions, polymerizations are usually conducted at higher temperatures and starved feed conditions to control copolymer composition and molecular weight (MW) while reducing the solvent level in the final product.[1] Previous studies indicate that methacrylate will undergo depropagation at the higher temperatures and low monomer concentrations, and that penultimate effects also affect polymerization rate and polymer molecular weight at elevated temperatures.[2–4] More recently, a mechanistic model including depropagation and penultimate effects provides a good fit to the experimental data for high temperature semibatch free radical copolymerization of butyl methacrylate (BMA) and styrene (ST).[5] This work will focus on the copolymerization of dodecyl methacrylate (DMA) and ST at similar reaction conditions, in order to improve general understanding of ST/methacrylate copolymerizations.

The same set of kinetic mechanisms and model structure developed for BMA/ST copolymerization should also hold true for the DMA/ST system. However, differences in rate coefficients must be considered. In comparison to BMA, the longer ester group of DMA increases the propagation rate constant[6] and contributes to a decrease in termination rate due to the stronger steric hindrance of the long-chain alkyl ester attached to the radical center.[7] Differences in initiator efficiency have also been reported,[8] which may affect the final polymer molecular weight at the same initiator level.

The aim of this paper is to investigate the copolymerization of DMA and styrene at high temperature and low monomer concentration and to demonstrate that the model structure established for ST/BMA can also be used for other ST/methacrylate copolymerization systems.

Experimental Part

DMA with 480–500 ppm of hydroquinone monomethyl ether (96% purity), and styrene (99% purity) inhibited with 10–15

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ppm of 4-*tert*-butylcatechol were purchased from Sigma Aldrich and used as received. *tert*-Butyl peroxyacetate (TBPA), provided as a solution of 75 wt% initiator in mineral spirits, and a xylene isomeric mixture with boiling point range between 136 and 140 °C were also obtained from Sigma Aldrich and used as received.

Table 1.
Kinetic mechanisms of high-temperature dodecyl methacrylate (1)/styrene (2) copolymerization.

Initiation	$I \xrightarrow{k_d} 2fI^{\bullet}$
	$I^{\bullet} + M_k \xrightarrow{k_{pkkk}} P_1^{k\bullet}$
Styrene self-initiation	$2M_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} DA$
	$DA + M_2 \xrightarrow{k_i} P_1^{2\bullet} + P_2^{2\bullet}$
Propagation	$P_n^{j\bullet} + M_k \xrightarrow{P_{ij}k_{p_{ijk}}} P_{n+1}^{k\bullet}$
Chain transfer to monomer	$P_n^{j\bullet} + M_k \xrightarrow{k_{tr_{jk}}^{mon}} P_1^{k\bullet} + D_n$
Chain transfer to solvent	$P_n^{j\bullet} + S \xrightarrow{C_{s,j}k_{p_{jjj}}} I^{\bullet} + D_n$
Termination	
by combination:	$P_n^{j\bullet} + P_r^{k\bullet} \xrightarrow{k_{tc_{jk}}} D_{n+r}$
by disproportionation:	$P_n^{j\bullet} + P_r^{k\bullet} \xrightarrow{k_{td_{jk}}} D_n + D_r$
Inhibition	$I^{\bullet} + Inh \xrightarrow{k_{inh}} D$
	$P_n^{j\bullet} + Inh \xrightarrow{k_{inh}} D_n$
Depropagation	$P_{n+1}^{1\bullet} \xrightarrow{P_{11}k_{dep}} P_n^{1\bullet} + M_1$

Semibatch reactions were performed in a 1 L LabMax reactor system with an agitator and reflux condenser, and with initiator and monomer feed rates and reaction temperature automatically controlled. The experimental recipes are the same as those used for the ST/BMA system.[5] The reactor was charged with 215 g solvent and brought up to the reaction temperature of 138 °C. Monomer mixtures (492 g total) and initiator solution (13.1 g total) were continuously fed at a fixed rate over 6 hours with initiator fed for an extra 15 minutes; the total TBPA charge was 2 wt% of the monomer charge. With this recipe, final polymer content was 70 wt% in solution at the end of the reaction. Samples of approximately 10 mL were drawn from the reactor at specified times into ice-cold 4-methoxyphenol (1 g/L) solution to terminate the reaction.

The residual monomer concentration in the samples was determined using a Varian CP-3800 gas chromatograph (GC) setup,

Table 2.
Rate coefficients and model parameters for dodecyl methacrylate (1)/styrene (2) copolymerization.

	Rate expression	Value at 138 °C	Ref.
Initiation	$k_d(s^{-1}) = 6.78 \times 10^{15} \exp(-17714/T)$	1.32×10^{-3}	[11]
	f	0.33–0.55	this work
Styrene self-initiation	$k_1(L \cdot mol^{-1} \cdot s^{-1}) = 3.5 \times 10^{-7}$	3.50×10^{-7}	[12]
	$k_i(L \cdot mol^{-1} \cdot s^{-1}) = 1.633 \times 10^6 \exp(-12020/T)$	3.25×10^{-7}	[13]
	$k_f(L^2 \cdot mol^{-2} \cdot s^{-1}) = 2.19 \times 10^5 \exp(-13800/T)$	5.73×10^{-10}	[14]
	$k_{-1}(s^{-1}) = k_1 k_i / k_f$	–	
Propagation	$k_{p_{111}}(L \cdot mol^{-1} \cdot s^{-1}) = 2.512 \times 10^6 \exp(-2526/T)$	5.38×10^3	[9]
	$k_{p_{222}}(L \cdot mol^{-1} \cdot s^{-1}) = 4.266 \times 10^7 \exp(-3910/T)$	3.16×10^3	[15]
	$r_1 = 0.45, r_2 = 0.57, s_1 = 0.59, s_2 = 0.33$	–	[16]
Termination	$k_{t_{11}}(L \cdot mol^{-1} \cdot s^{-1}) = 8.32 \times 10^7 \exp(-601/T)$	1.93×10^7	[17,18]
	$k_{t_{22}}(L \cdot mol^{-1} \cdot s^{-1}) = 3.18 \times 10^9 \exp(-958/T)$	3.09×10^8	[19]
	$k_{t,cop}(L \cdot mol^{-1} \cdot s^{-1}) = k_{td_{ij}} + k_{tc_{ij}}$		this work
	$k_{td_{11}}/k_{t,cop} = 0.65; k_{td_{22}}/k_{t,cop} = 0.01; k_{td_{12}}/k_{t,cop} = 0.33^{a)}$		
Inhibition	$k_{inh}(L \cdot mol^{-1} \cdot s^{-1})$	1.0×10^9	this work
Transfer to solvent	$C_{s,1} = 5.55 \exp(-4590/T)^{\#}$	7.87×10^{-5}	
	$C_{s,2}$	1.00×10^{-4}	[20]
Transfer to monomer	$k_{tr_{11}}^{mon}(L \cdot mol^{-1} \cdot s^{-1}) = 1.56 \times 10^2 \exp(-2621/T)^{\#}$	0.27	[21]
	$k_{tr_{22}}^{mon}(L \cdot mol^{-1} \cdot s^{-1}) = 2.31 \times 10^6 \exp(-6377/T)$	0.427	[14]
	$k_{tr_{ij}}^{mon}(i \neq j) = k_{tr_{jj}}^{mon} \frac{k_{p_{ij}}}{k_{p_{jj}}}$	–	[1]
Depropagation	$k_{dep}/k_{p_{111}} = [M]_{eq} = 2.66 \times 10^6 \exp(-6571/T)$		[22]
Density	$\rho_{DMA}(kg \cdot L^{-1}) = 0.88794 - 7.57 \times 10^{-4} T(^{o}C)$	0.782	[23]
	$\rho_{ST}(kg \cdot L^{-1}) = 0.9193 - 6.65 \times 10^{-4} T(^{o}C)$	0.827	[5]
	$\rho_{pol}(kg \cdot L^{-1}) = 1.19 - 8.07 \times 10^{-4} T(^{o}C)$	1.079	[5]

a) Assumed equal to Butyl Methacrylate value (see reference 5).

as detailed before.[5] Calibration standards were constructed by mixing measured quantities of styrene and DMA monomers into a known mass of acetone, and a linear calibration curve was constructed by plotting peak area versus monomer concentration.

Size-exclusion chromatography (SEC) analyses of the polymer samples were performed using a Waters 2960 separation module with a Waters 410 differential refractometer (RI detector) and a Wyatt Technology Light Scattering detector (LS detector). Calibration for the RI detector was establish using 8 linear narrow PDI polystyrene standards over a large range of molecular weight, from 890 to 3.55×10^5 g/mol, and the MW of the copolymers and poly(DMA) can be obtained by universal calibration using known Mark-Houwink parameters.[9] The output signal of LS detector provides the absolute molar mass without the need for calibration standards but with knowledge of the *dn/dc* value

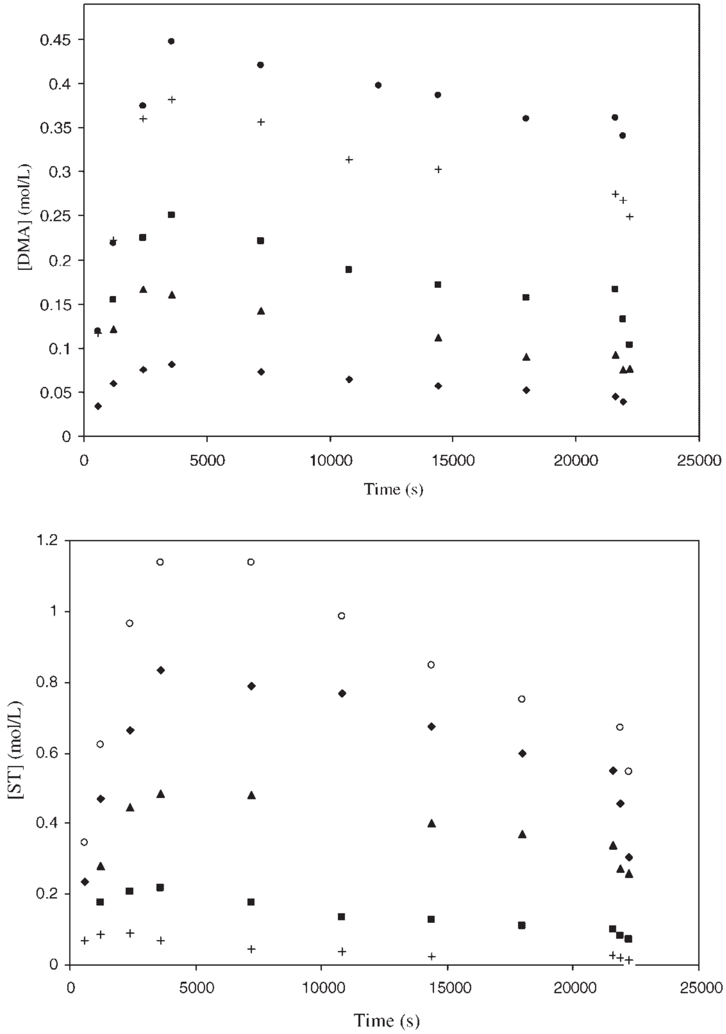

Figure 1.
[DMA] (top) and [ST] (bottom) semibatch experimental profiles: ST homopolymerization (○); ST/DMA 75/25 copolymerization (◆); ST/DMA 50/50 copolymerization (▲); ST/DMA 25/75 copolymerization (■); ST/DMA 10/90 copolymerization (+); DMA homopolymerization (●).

$((dn/dc)_{ST} = 0.18, (dn/dc)_{DMA} = 0.0544^{[10]})$. MW averages from the two detectors (presented later) are within 15% of each other.

Model and Kinetics for Copolymerization of ST/DMA

Since DMA and BMA belong to the same family of monomers, and are polymerized with styrene under the same reaction conditions and recipes, similar reactions and mechanisms will occur. The model includes initiation, styrene thermal initiation, propagation (including penultimate chain-growth effects), depropagation, transfer to monomer and solvent, and termination, as shown in Table 1. Depropagation only occurs with methacrylate units in both the penultimate and terminal positions of the polymer radicals,[5] and P_{ij} represents the probability of having penultimate unit i attached to terminal radical j, and is calculated as detailed in previous work.[2,5] Inhibition is also included in the model, with the termination coefficient for inhibition (k_{inh}) set to 1.0×10^9 L/(mol·s), as

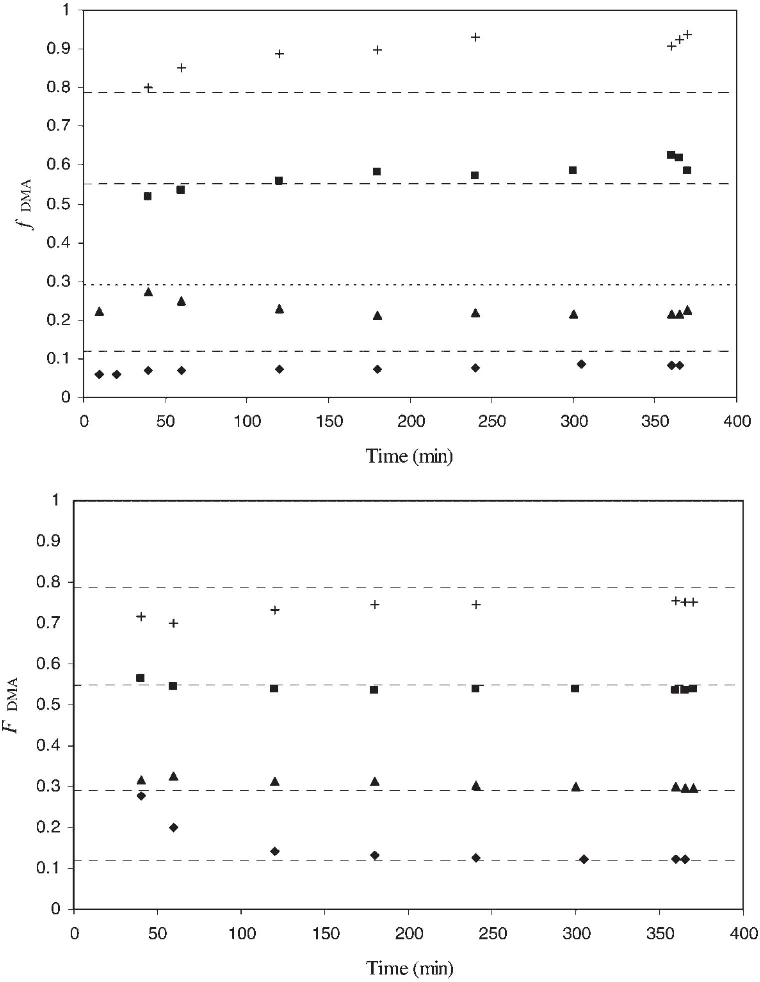

Figure 2.

Monomer mole fraction (top) and cumulative copolymer composition (bottom) in the semibatch DMA/ST copolymerizations, as determined from GC measurement of residual monomer and calculated by mass balance for the feed ratios (wt%): DMA/ST 90/10 (+); DMA/ST 75/25 (■); DMA/ST 50/50 (▲); DMA/ST 25/75 (◆). Horizontal lines indicate the monomer feed ratio converted to a molar basis.

inhibitor is very effective in scavenging radicals in the system. Even with the high inhibitor level in the DMA, the initiator levels are significantly higher such that less than 3% of the initiator is consumed by inhibition.

The rate coefficients for DMA/ST copolymerization are summarized in Table 2. As mentioned previously, the values of k_p[9] and k_t[17,18] of DMA differ from those of BMA due to the longer ester group of DMA. The equilibrium monomer concentration ($[M]_{eq}$) of DMA, required for the treatment of depropagation, is deduced from reference 22. For BMA, the value of $[M]_{eq}$ was written as a function of temperature and of polymer weight fraction in the system, based on experimental studies.[21] As similar studies have not been performed for DMA, it was decided to adopt a simpler treatment, with $[M]_{eq}$ only a function of temperature as outlined in Table 2. Our previous kinetic study of ST/BMA indicated that methacrylate/styrene monomer and radical reactivity ratios are independent of temperature over a wide range;[3] thus ST/DMA values measured at 25 °C[16] are used in the model. Transfer coefficients to solvent and monomer and the fraction of termination by disproportionation vs. combination for DMA are assumed to be the same as for BMA. The initiator efficiency f is estimated by fitting experimental monomer concentration and polymer molecular weight profiles simultaneously, as described later.

Results and Discussion

ST/DMA semibatch experiments were run with monomer mass feed ratios of 100/0, 75/25, 50/50, 25/75, 10/90, 0/100; the free monomer concentration profiles in the reactor are plotted in Figure 1. Figure 2 shows the relative molar composition of free monomer in the reactor and of the cumulative copolymer composition, as calculated using mass balances. The low monomer concentations (Figure 1) and the constant polymer compositions during polymerization (Figure 2) are characteristic of starved-feed operation, which can effectively control the final polymer composition to be essentially identical to the feed composition. The azeotrope composition for DMA/ST copolymerization is calculated as $f_{\mathrm{DMA}} = 0.44$, using the reactivity ratio values in Table 2. Thus, DMA is preferentially incorporated into the

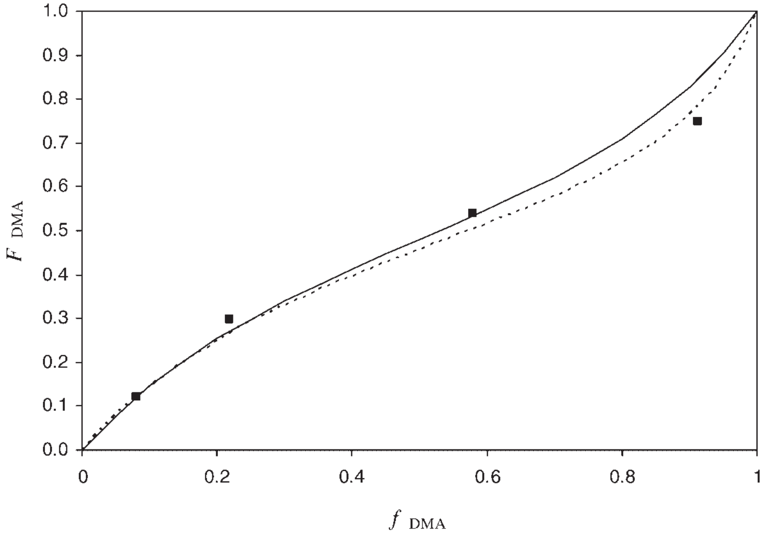

Figure 3.
DMA polymer composition vs. f_{DMA} (mole fraction) in the semibatch reactions at 138 °C: experiment (■); Mayo-Lewis model (—); Lowry Case 1 model with $[M]_{tot} = 0.5$ mol/L (- - -).

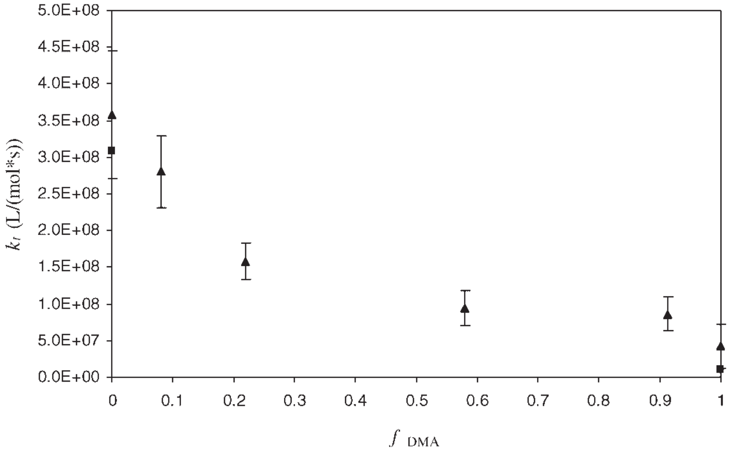

Figure 4.
Termination rate coefficients for DMA/ST copolymerization vs. DMA monomer fraction, estimated by assuming penultimate propagation (▲) kinetics. Error bar indicates estimated confidence intervals from parameter fitting. Homopolymerization k_t values from the literature (■) are also shown.

copolymer at low DMA fraction so that f_{DMA} is less than the DMA fraction in the feed (DMA/ST mass feed ratios of 25/75 and 50/50), as shown in Figure 2, while ST is preferentially incorporated into the copolymer at higher DMA fractions.

Methacrylates undergo significant depropagation at temperatures higher than 120 °C, which in turn influences copolymer composition.[5] In order to investigate the effect of the depropagation on composition, the Mayo-Lewis model[24] (without depropagation) and the Lowry Case 1 depropagation model[2] with 0.5 mol/L in total monomer concentration, a value selected according to Figure 1, are compared with the experimental results, as shown in Figure 3. As also found for the BMA/ST copolymer system,[5] depropagation has a negligible effect on polymer composition at low DMA mole fractions; the monomer reactivity ratio values of less than unity promote an alternating copolymer structure. However, at high DMA mole fractions, DMA depropagation is stronger and the Lowry Case 1 model gives a better prediction of the polymer composition.

As mentioned in our previous paper,[5] k_t values for copolymerization ($k_{t,cop}$) are not available in literature and must be estimated from the experimental data. Because of the low polymer MWs and high reaction temperature, the viscosity of the system is low during the polymerization process and so the termination process is controlled by segmental diffusion. Thus, $k_{t,cop}$ can be assumed constant for each experiment and is estimated using experimental monomer concentrations. The $k_{t,cop}$ estimation approach was validated in our previous paper[5] and the good match between the estimated k_t for ST and DMA homopolymerization and k_t from the literature in Figure 4 verify the validity of the approach for this system as well.

Table 3.
Experimental and simulated final polymer weight-average MWs. Simulated values show the effect of the fraction of methacrylate termination by disproportion (f_{disp}).

wt% DMA in the feed	Experimental MW ($g \cdot mol^{-1}$)		Simulated MW($g \cdot mol^{-1}$)	
	RI Detector	LS Detector	$f_{disp} =$ 0.65	$f_{disp} =$ 0
100	17 800	17 400	10 700	12 600
90	22 500	21 500	14 200	16 800
75	24 800	21 900	15 800	16 300
50	29 000	25 300	16 700	16 900
25	21 400	20 200	17 300	17 200
0	14 800	16 900	17 600	17 600

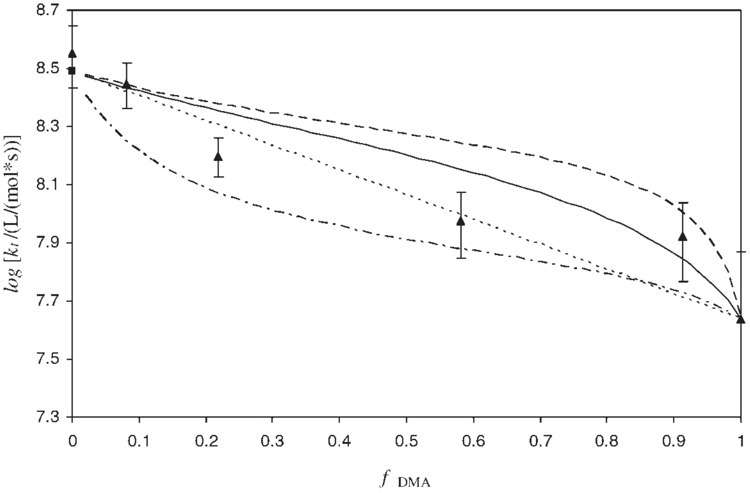

Figure 5.
Termination rate coefficients for DMA/ST copolymerization vs. DMA monomer mole fraction: estimated values (▲); Walling equation (—); Atherton and North model (— —); Buback simplified model (- - -); Ma model (— - —). Error bar indicates estimated confidence intervals from parameter fitting.

Using the estimated $k_{t,cop}$ values with the other kinetic coefficients summarized in Table 2 ($f = 0.515$) leads to a significant discrepancy between simulated weight-average MW values and those measured experimentally, as shown in Table 3. Polydispersities for these samples were narrow (1.6–2.0), as also observed for ST/BMA starved-feed copolymerization.[5] Note that the experimental measures from the two detectors (RI and LS) are in excellent agreement, such that the mismatch from simulated values cannot be attributed to calibration issues. In addition, eliminating all chain transfer reactions from the model only raises the predicted MW values slightly (not shown); with such high initiator levels in the system, MW is predominantly controlled by termination. Even decreasing the fraction of methacrylate termination

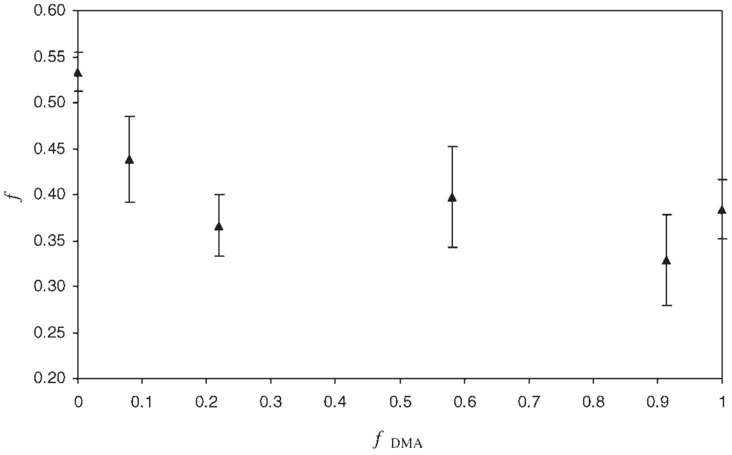

Figure 6.
Initiator efficiencies (f) estimated for DMA/ST copolymerization vs. DMA monomer mole fraction. Error bar indicates estimated confidence intervals from parameter fitting.

that occurs by disproportionation (f_{disp}) to zero from 0.65 (set according to the previous ST/BMA work, as no literature value was found for DMA) does not raise the simulated MW values sufficiently to match those measured experimentally, as summarized in Table 3.

Another potential cause of the mismatch in MW may be the initiator efficiency (f), as MW is proportional to $\left(\frac{1}{fk_{t,cop}}\right)^{0.5}$. To explore this possibility further, the experimental weight-average MW values were used to estimate the initiator efficiencies in Predici®. Since polymerization rate is proportional to $\left(\frac{f}{k_{t,cop}}\right)^{0.5}$, the change in f will also influence predictions of free monomer in the reactor. Thus, $k_{t,cop}$ and f were estimated simultaneously from the experimental

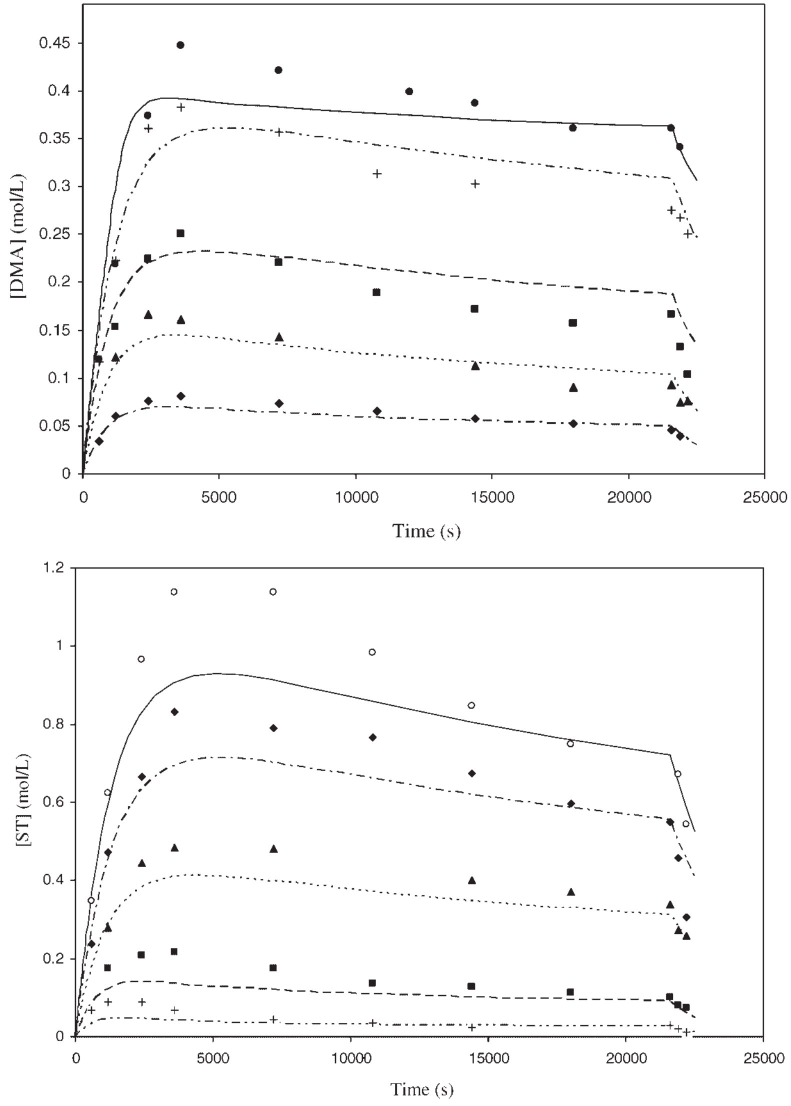

Figure 7.
[DMA] (top) and [ST] (bottom) semibatch experimental profiles (points) and model predictions (lines): ST homopolymerization (○,——); ST/DMA 75/25 copolymerization (◆,— - —); ST/DMA 50/50 copolymerization (▲,- - -); ST/DMA 25/75 copolymerization (■,— —); ST/DMA 10/90 copolymerization (+,— - - —); DMA homopolymerization (●,——).

monomer concentration and M_w profiles using the parameter estimation capabilities of Predici®. The estimated $k_{t,cop}$ and f values are shown in Figure 5 and 6.

The simultaneous fitting made little change to the estimated $k_{t,cop}$ values; those in Figure 5 are very close to the values shown in Figure 4. The data in Figure 5 are plotted on a logarithmic scale, to facilitate comparison to various models (Walling equation,[25] Atherton and North diffusion model,[26] Ma modified diffusion model,[27] and Buback simplified model[28]) proposed in the literature for $k_{t,cop}$, represented by the lines in the plot. Walling's equation assumes that termination is chemically controlled, while the other three models are formulated assuming that the termination rate coefficient is controlled by diffusion. Figure 5 indicates that the Buback simplified model provides a slightly better prediction of the estimated $k_{t,cop}$ values than the others. This finding is in accordance with the ST/BMA copolymerization system[5] and suggests that the Buback simplified model might be generally adopted for $k_{t,cop}$ calculation for such copolymerization systems.

Figure 6 plots the estimates of initiator efficiency (f) as a function of DMA mole fraction in the monomer mixture in the reactor (f_{DMA}). The initiator efficiency decreases from 0.53 to 0.44 when f_{DMA} increases from 0 (ST homopolymerization) to 0.25, and remains relatively constant, within the indicated error bars from the parameter estimation, as f_{DMA} increases further. There are two reasons that can be put forth to explain this result. The first is that the total monomer concentration decreases as the proportion of DMA increases, even though the mass of DMA and ST fed to the reactor is kept constant. The decrease of the total monomer concentration has been shown to result in the decrease of initiator efficiency,[29] and initiator efficiency with DMA systems has been measured as lower relative to other methacrylates.[8]

Table 4.
Experimental and simulated final polymer weight-average MWs.

wt% DMA in the feed	Experimental MW (g · mol^{-1}) RI Detector	Experimental MW (g · mol^{-1}) LS Detector	Simulated MW(g · mol^{-1})
100	17 800	17 400	16 700
90	22 500	21 500	21 300
75	24 800	21 900	19 100
50	29 000	25 300	22 900
25	21 400	20 200	20 000
0	14 800	16 900	16 900

Figure 7 compares experimental data to the penultimate model predictions using the estimated $k_{t,cop}$ and f values. The experimental data and the predicted curves for both [DMA] and [ST] are in good accordance. Table 4 compares the experimental final weight-average MW (M_w) values to the model predictions. M_w values for the ST/DMA system first increase as styrene content in the reactor feed decreases from 100 to 50 wt%, and then decrease with the further decrease of styrene content. This trend reflects a balance between changing initiator efficiency and the large difference between the molecular weights of ST and DMA monomers. The model captures this behavior, but not quite to the same extent as observed experimentally.

Conclusion

High temperature semibatch ST/DMA free radical copolymerization was investigated over the complete range of copolymer composition. The trends observed are similar to those found for ST/BMA copolymerization under similar starved-feed operating conditions. The MW results suggest that initiator efficiency for the ST/DMA copolymerization system is lower than that found for the corresponding ST/BMA system. The ST/methacrylate mechanistic model developed previously provides a good representation of the experimental observations, after accounting for the difference in BMA and DMA rate coefficients and fitting copolymer-averaged termination rate coefficient and initiator efficiency values to the data.

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