High Temperature Semibatch Free Radical Copolymerization of Styrene and Butyl Acrylate

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Summary: High temperature semibatch free radical solution copolymerizations of *n*-butyl acrylate (BA) and styrene (ST) were carried out over a range of copolymer composition. The significant increase in experimental polymer weight-average molecular weight with time, as well as the shift in the entire polymer molecular weight distribution, is explained by assuming fast β-scission of BA midchain radicals with an adjacent styrene unit, followed by subsequent addition of the resultant macromonomer to growing radicals. A mechanistic model including backbiting and β-scission, macronomer incorporation, long-chain branching, and propagation and termination penultimate effects was constructed in Predici; the model provides a good representation of the experimental data using rate coefficients taken from literature.

Keywords: butyl acrylate; copolymerization; kinetics (polym.); modeling; styrene

Introduction

Copolymers of acrylate and styrene (ST) 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] In free radical polymerization of acrylates, it is now well-accepted that the propagating secondary *n*-butyl acrylate (BA) radical can undergo backbiting (intramolecular chain transfer to polymer) even at ambient temperature to form midchain radicals that can then subsequently propagate or terminate,[2] or, at higher temperatures, form macromonomer via β-scission.[3] Our recent study[4] of high temperature semibatch BA homopolymerization indicated that macromonomer formed in the system is almost as reactive as monomer, with the ratio of the propagation rate coefficient of macromonomer (k_{mac}) and monomer (k_p) estimated as $k_{mac}/k_p = 0.55$.

Numerous papers can be found in the literature[5] dealing with lower temperature free radical copolymerization of BA and ST. The presence of ST monomer slows down the polymerization rate[5a,5b] and also decreases the gel content.[5i] Copolymer composition is well-described by the terminal model,[5a,5b] with monomer reactivity ratios showing some temperature dependency,[5c,5h] fit to the Arrhenius relationships $\ln r_1 = 0.05919 - 131.6/T(\mathrm{K})$ and $\ln r_2 = 1.3510 - 1034.1/T(\mathrm{K})$,[5h] with r_1 and r_2 representing the monomer reactivity ratios of ST and BA, respectively. The terminal model, however, fails to represent both copolymer composition and copolymerization propagation rate simultaneously for ST/methyl acrylate (MA) and ST/BA systems, with styrene units in the penultimate position largely responsible for the reduced rate relative to terminal model predictions.[5j] The literature values for ST/BA monomer and radical reactivity ratios have been shown to provide a good

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description of terpolymerization propagation kinetics, with butyl methacrylate (BMA) as the third monomer.[6]

In addition to modeling the effect of penultimate units, the backbiting and β-scission reactions prevelant in acrylate systems,[2,3,4] especially at higher temperatures, must be considered. Some of these reactions have been described in our previous study of the BA/BMA system at 138 °C,[7] and Plessis et al.[5i] have consider the impact of ST comonomer on acrylate backbiting. The aim of this paper is to investigate the copolymerization kinetics of ST/BA at high temperature and low monomer concentration, conditions used to manufacture acrylic resins for coatings applications. In addition to a complete description of backbiting and β-scission, it is necessary to consider the reactivity of the macromonomers formed by β-scission in order to completely describe the evolution of polymer weight-average molecular weights (M_w) and molecular weight distributions (MWD) with polymerization time.

Experimental Part

Materials

BA with 10 ppm of methyl ether of hydroquinone (99% purity), and styrene (99% purity) inhibited with 10-15 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 by Arkema, and a xylene isomeric mixture with boiling point range between 136 and 140 °C obtained from Sigma Aldrich were used as received.

Semibatch Experiments

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 were the same as those used for the ST/BMA,[8] BMA/BA[7] and ST/dodecyl methacrylate (DMA) systems.[1] The reactor was charged with 215 g xylene 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 2∼3 mL were drawn from the reactor at specified times into ice-cold solution of 4-methoxyphenol ($1\,g \cdot L^{-1}$) in xylene to terminate the reaction.

Characterization

The residual monomer concentration in the samples was determined using a Varian CP-3800 gas chromatograph (GC) setup, as detailed before.[1] Calibration standards were constructed by mixing measured quantities of styrene and BA 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). Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1 mL/min, and Styragel packed columns HR 0.5, HR 1, HR 3 and HR 4 (Waters Division Millipore) were used. Calibration for the RI detector was established using 8 linear narrow PDI polystyrene standards covering a molecular weight range from 890 to $3.55 \times 10^5\ g \cdot mol^{-1}$; the MW of the copolymers and poly(BA) were obtained by universal calibration using known Mark-Houwink parameters ($K_{ST} = 1.14 \times 10^{-4}\,mL \cdot g^{-1}$ and $a_{ST} = 0.716$;[9] $K_{BA} = 12.2 \times 10^{-3}\,mL \cdot g^{-1}$ and $a_{BA} = 0.70$[10]).

Model and Kinetics for Copolymerization of ST/BA

The mechanistic model developed for free radical copolymerization of ST/BA is based on our previous BMA/BA model,[7] with the addition of intermolecular chain transfer to BA units in the copolymer chains (long chain branching, or LCB)[15] and radical addition to macromonomer chains formed via β-scission.[4] A BA unit in the polymer chain can also be attacked by oxygen-centered radicals formed from initiator decomposition.[1,4]

The complete set of mechanisms implemented in Predici[11] includes initiation, propagation, chain transfer to monomer and solvent, intermolecular chain transfer to poly(BA), termination, backbiting (intramolecular chain transfer to poly(BA)), β-scission, and macromonomer propagation, as shown in Table 1. For this two-monomer BA (1)/ ST (2) system, two types of chain-end radicals are defined, denoted by $\mathrm{P_n^{1\bullet}}$ and $\mathrm{P_n^{2\bullet}}$, with the subscript-n representing chain length. $\mathrm{Q_n^{ijk\bullet}}$ represents the midchain radicals (with terminal units ijk) formed by backbiting, and $\mathrm{U_n}$ is a macromonomer with chain length of n. Inhibition is neglected in the model, as the inhibitor is present at levels less than 0.05% of the initiator. In addition, the self-initiation of ST at 138 °C can be safely neglected for this system, as the radical concentration generated from initiator (added at a level of 2 wt% relative to monomer) is orders of magnitude higher. The initiator efficiency *f*, set at 0.5 in accordance with our previous modeling,[3b,4] represents the fraction of radicals successful in initiating polymerization. The complete set of coefficients used in the model, along with literature sources, is listed in Table 2.

As shown in our kinetic study of the BMA/ST/BA system,[6] penultimate propagation kinetics must be considered. For ST/BA, there are eight monomer addition reactions when considering the penultimate unit of the radicals, and two backbiting reactions of BA radicals with pen-penultimate BA unit, as shown in Scheme 1. $k_{\mathrm{p_{ijk}}}$is the rate coefficient for addition of monomer *k* to radical *ij*, leading to the following definitions of monomer (r_i) and radical (s_i) reactivity ratios for the implicit penultimate propagation model:[13]

$$\begin{aligned} r_1 &= k_{\mathrm{p_{111}}}/k_{\mathrm{p_{112}}} = k_{\mathrm{p_{211}}}/k_{\mathrm{p_{212}}}; \quad s_1 = k_{\mathrm{p_{211}}}/k_{\mathrm{p_{111}}} \\ r_2 &= k_{\mathrm{p_{222}}}/k_{\mathrm{p_{221}}} = k_{\mathrm{p_{122}}}/k_{\mathrm{p_{121}}}; \quad s_2 = k_{\mathrm{p_{122}}}/k_{\mathrm{p_{222}}} \end{aligned} \tag{1}$$

To reduce the number of species in the model, two types of chain-end radicals are defined, $\mathrm{P_n^{1\bullet}}$ and $\mathrm{P_n^{2\bullet}}$. The symbol P_{ij} represents the fraction of radical-*j* with unit-*i* present in the penultimate position, and is introduced to track the penultimate unit in a terminal radical. Thus,

$$\begin{aligned} \mathrm{P^{11\bullet}} &= P_{11}\mathrm{P^{1\bullet}}, \qquad \mathrm{P^{22\bullet}} = P_{22}\mathrm{P^{2\bullet}} \\ \mathrm{P^{21\bullet}} &= P_{21}\mathrm{P^{1\bullet}}, \qquad \mathrm{P^{12\bullet}} = P_{12}\mathrm{P^{2\bullet}} \end{aligned} \tag{2}$$

where $\mathrm{P}^{j\bullet}$ represents all radicals ending in repeat unit *j* ($\mathrm{P}^{j\bullet} = \sum_{n=1}^{\infty} \mathrm{P_n}^{j\bullet}$) and $\mathrm{P}^{ij\bullet}$ represents all radicals ending in *ij* ($\mathrm{P}^{ij\bullet} = \sum_{n=1}^{\infty} \mathrm{P_n}^{ij\bullet}$). From the definitions, it is clear that $P_{11} + P_{21} = 1$ and $P_{22} + P_{12} = 1$. The probabilities, required for the penultimate propagation model (Scheme 1), are calculated by applying the long chain hypothesis and steady state assumption to the radical balances:[14]

$$P_{11} = k_{\mathrm{p211}}[\mathrm{M_1}]/(k_{\mathrm{p112}}[\mathrm{M_2}] + k_{\mathrm{p211}}[\mathrm{M_1}]) \tag{3}$$

$$P_{22} = k_{\mathrm{p122}}[\mathrm{M_2}]/(k_{\mathrm{p122}}[\mathrm{M_2}] + k_{\mathrm{p221}}[\mathrm{M_1}]) \tag{4}$$

In addition, penultimate effects are also considered for radical-radical termination, as described in previous work[1] and represented by Eq. 5:

$$\begin{aligned} k_{\mathrm{t,cop}}^{0.5} &= k_{\mathrm{t\,11,11}}^{0.5}P_{11} + k_{\mathrm{t\,21,21}}^{0.5}P_{21} \\ &\quad + k_{\mathrm{t\,22,22}}^{0.5}P_{22} + k_{\mathrm{t\,12,12}}^{0.5}P_{12}; \\ k_{\mathrm{t\,ij,kl}} &= (k_{\mathrm{t\,ij,ij}}k_{\mathrm{t\,kl,kl}})^{0.5} \end{aligned} \tag{5}$$

Similar to the BA/BMA system,[7] backbiting will occur only when an acrylate

Table 1.
Kinetic mechanisms included in the model of high-temperature styrene (1)/butyl acrylate (2) copolymerization.

Initiation	$I \xrightarrow{k_d} 2f\, I^\bullet$
	$I^\bullet + M_j \xrightarrow{k_{p_{jj}}} P_1^{j\bullet}$
Propagation	$P_n^{i\bullet} + M_j \xrightarrow{k_{p_{ij}}} P_{n+1}^{j\bullet}$
Chain transfer to monomer	$P_n^{i\bullet} + M_j \xrightarrow{k_{tr_{ij}}^{mon}} P_1^{j\bullet} + D_n$
Chain transfer to solvent	$P_n^{i\bullet} + S \xrightarrow{C_{s,i} k_{p_{ii}}} I^\bullet + D_n$
Termination	
by combination	$P_n^{i\bullet} + P_r^{j\bullet} \xrightarrow{k_{tc_{ij}}} D_{n+r}$
by disproportionation	$P_n^{i\bullet} + P_r^{j\bullet} \xrightarrow{k_{td_{ij}}} D_n + D_r$
Backbiting	$P_n^{2\bullet} \xrightarrow{P_{22} P_{22} k_{bb}} Q_n^{222\bullet}$
	$P_n^{2\bullet} \xrightarrow{0.6 P_{21} P_{12} k_{bb}} Q_n^{212\bullet}$
β-scission	$Q_n^{222\bullet} \xrightarrow{k_\beta} U_{n-2} + P_2^{2\bullet}$
	$Q_n^{222\bullet} \xrightarrow{P_{22} k_\beta} U_3 + P_{n-3}^{2\bullet}$
	$Q_n^{222\bullet} \xrightarrow{P_{12} f_{ST} k_\beta} U_3 + P_{n-3}^{1\bullet}$
	$Q_n^{212\bullet} \xrightarrow{f_{ST} k_\beta} U_{n-2} + P_2^{1\bullet}$
	$Q_n^{212\bullet} \xrightarrow{P_{22} k_\beta} U_3 + P_{n-3}^{2\bullet}$
	$Q_n^{212\bullet} \xrightarrow{P_{12} f_{ST} k_\beta} U_3 + P_{n-3}^{1\bullet}$
Macromonomer propagation#	$P_n^{2\bullet} + U_r \xrightarrow{k_{mac}} Q_{n+r,L}^\bullet$
	$P_n^{1\bullet} + U_r \xrightarrow{0.55 \times k_{p_{11}} / r_{ST,BMA}} Q_{n+r,L}^\bullet$
Short-chain branching	$Q_n^\bullet + M_i \xrightarrow{k_p^t \times r_i / r_2} P_{n+1}^{i\bullet}$
Long-chain branching#,&	$I^\bullet + D_n \xrightarrow{n \times F_2 \times k_{trP}^{I^\bullet}} Q_{n,L}^\bullet + D_1$
	$P_n^{2\bullet} + D_r \xrightarrow{r \times F_2 \times k_{trP}} Q_{r,L}^\bullet + D_n$
Termination of tertiary radicals	
by combination	$Q_n^\bullet + Q_r^\bullet \xrightarrow{k_{tc22}^t} D_{n+r};\ Q_n^\bullet + P_r^{j\bullet} \xrightarrow{(k_{tc2j}^t \times k_{tc2j})^{0.5}} D_{n+r}$
by disproportionation	$Q_n^\bullet + Q_r^\bullet \xrightarrow{k_{td22}^t} D_n + D_r;\ Q_n^\bullet + P_r^{j\bullet} \xrightarrow{(k_{td2j}^t \times k_{td2j})^{0.5}} D_n + D_r$

#, the midchain radicals formed by macromonomer propagation and intermolecular chain transfer to polymer can also undergo propagation by monomer addition and termination, as shown for midchain radicals formed by backbiting;

& F_2 represents the BA mole fraction in the polymer chain; long chain branching reactions involving macromonomer (U_n) are also allowed to occur.

radical finds an acrylate unit in its penpenultimate position. However, the reaction can occur if either a BA or ST unit is in the penultimate position, with the backbiting rate reduced by a factor of 0.6 if styrene (Scheme 2b) is in the adjacent position compared to butyl acrylate (Scheme 2a), as estimated by ^{13}C-NMR analysis (not shown) of the amount of quarternary carbon of the resultant BA/ST copolymers. This result is consistent with Plessis et al.'s work on BA/ST copolymerization indicating that the rate of backbiting of BA radical with styrene as the adjacent unit is lower than the rate with adjacent BA.[24]

The midchain radicals generated by backbiting can terminate, propagate, or undergo β-scission to form macromonomers and radicals (Scheme 3). As discussed previously,[7] the rate of β-scission depends

Table 2.
Model Rate coefficients and Parameters.

	rate expression	ref
Initiation	$k_d(s^{-1}) = 6.78 \times 10^{15} \exp(-17714/T)$	[16]
Propagation	$k_{p11}(L \cdot mol^{-1} \cdot s^{-1}) = 4.266 \times 10^7 \exp(-3910/T)$	[17]
	$k_{p22}(L \cdot mol^{-1} \cdot s^{-1}) = 1.8 \times 10^7 \exp(-2074/T)$	[18]
	$\ln r_1 = 0.05919 - 131.6/T(K)$	[5c]
	$\ln r_2 = 1.3510 - 1034.1/T(K)$	
	$s_1 = 0.11; \quad s_2 = 0.9$	[5j]
Termination	$k_{t11}(L \cdot mol^{-1} \cdot s^{-1}) = 3.18 \times 10^9 \exp(-958/T)$	[19]
	$k_{t22}(L \cdot mol^{-1} \cdot s^{-1}) = 5.14 \times 10^8 \exp(-480/T)$	[19]
	$k_{t,cop}^{0.5} = k_{t\,11,11}^{0.5} p_{11} + k_{t\,21,21}^{0.5} p_{21} + k_{t\,22,22}^{0.5} p_{22} + k_{t\,12,12}^{0.5} p_{12}$	[1]
	$k_{t\,ij,kl} = (k_{t\,ij,ij} k_{t\,kl,kl})^{0.5}$	
	$k_{td11}/k_{t,cop} = 0.01; \quad k_{td22}/k_{t,cop} = 0.05; \quad k_{td12}/k_{t,cop} = 0.03$	[20]
	$k_t^t(L \cdot mol^{-1} \cdot s^{-1}) = 1.8 \times 10^7 \exp(-673/T)$	[18]
Backbiting	$k_{bb} = 7.41 \times 10^7 \exp(-3933/T)$	[15b]
β-scission	$k_\beta = 12\ s^{-1}$ at 138 °C	[4]
	$f_{ST} = 50$	this work
Macromonomer propagation#	$k_{mac}/k_{p22} = 0.55$	[4]
Short-chain branching	$k_p^t = 1.2 \times 10^6 \exp(-3440/T)$	[21]
Long-chain branching	$k_{trP}^{l\bullet}/k_{p22} = 0.01$	[1]
	$k_{trP} = 4.01 \times 10^3 \exp(-3488/T)$	[2i]
Transfer to monomer	$k_{tr11}^{mon}(L \cdot mol^{-1} \cdot s^{-1}) = 2.31 \times 10^6 \exp(-6377/T)$	[22]
	$k_{tr22}^{mon}(L \cdot mol^{-1} \cdot s^{-1}) = 2.88 \times 10^5 \exp(-3922/T)$	[23]
Transfer to solvent	$C_{trS,1} = 8.0 \times 10^{-4}$ at 138 °C	[1]
	$C_{trS,2} = 2.0 \times 10^{-3}$ at 138 °C	[4]

$$\begin{array}{ll}
P_n^{1\bullet} + M_1 \xrightarrow{P_{11}k_{p111}} P_{n+1}^{1\bullet} & P_n^{1\bullet} + M_1 \xrightarrow{P_{21}k_{p211}} P_{n+1}^{1\bullet} \\
P_n^{1\bullet} + M_2 \xrightarrow{P_{11}k_{p112}} P_{n+1}^{2\bullet} & P_n^{1\bullet} + M_2 \xrightarrow{P_{21}k_{p212}} P_{n+1}^{2\bullet} \\
P_n^{2\bullet} + M_2 \xrightarrow{P_{12}k_{p122}} P_{n+1}^{2\bullet} & P_n^{2\bullet} + M_2 \xrightarrow{P_{22}k_{p222}} P_{n+1}^{2\bullet} \\
P_n^{2\bullet} + M_1 \xrightarrow{P_{12}k_{p121}} P_{n+1}^{1\bullet} & P_n^{2\bullet} + M_1 \xrightarrow{P_{22}k_{p221}} P_{n+1}^{1\bullet} \\
P_n^{2\bullet} \xrightarrow{P_{22}P_{22}k_{bb}} Q_n^{222\bullet} & P_n^{2\bullet} \xrightarrow{P_{21}P_{12}k_{bb}} Q_n^{212\bullet}
\end{array}$$

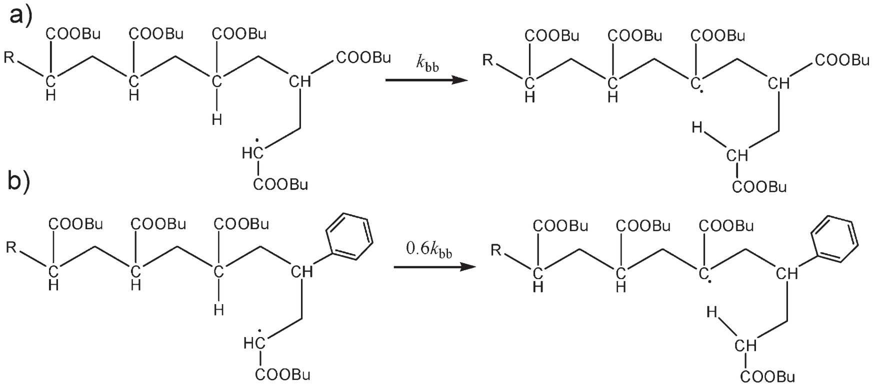
Scheme 1.
Penultimate propagation kinetic scheme for styrene (1)/butyl acrylate (2) copolymerization.

on the identity of the units adjacent to the acrylate midchain radical; the formation of ST radical should be favored over BA, due to the greater radical stability. The ratio of these two β-scission reactions, denoted by f_{ST}, was estimated as 50 in this work in order to match the significant increase in polymer weight-average molecular weight (M_w) observed experimentally, as discussed below.

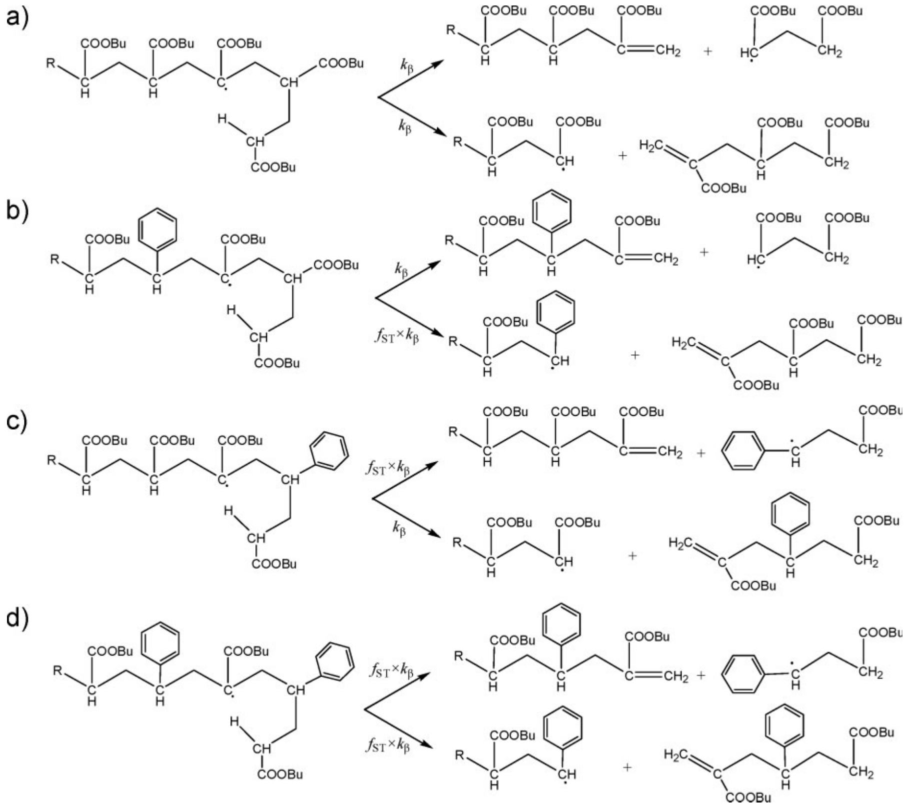
The macromonomers generated from β-scission (Scheme 3) are as reactive as monomer, and the significance of macromonomer reactions under high temperature monomer starved feed conditions was illustrated elsewhere.[4] The implementation of macromonomer reactions is simplified as follows:

$$P_n^{2\bullet} + U_r \xrightarrow{k_{mac}} Q_{n+r,L}^{\bullet} \tag{6}$$

$$P_n^{1\bullet} + U_r \xrightarrow{0.55 \times k_{p11}/r_{ST,BMA}} Q_{n+r,L}^{\bullet} \tag{7}$$



Scheme 2.
Backbiting (intramolecular chain transfer) of butyl acrylate propagating radicals with butyl acrylate (a) and styrene (b) as penultimate unit to form midchain radicals.



Scheme 3.
β-scission of midchain radicals formed by backbiting to create macromonomers and macroradicals.

where k_{mac}/k_{p22} was previously estimated as 0.55 at 138 °C;[4] and the addition rate of macromonomer to ST radical can be reasonably written as $0.55 \times k_{p_{11}}/r_{ST,BMA}$. The subscript L is added to the description of these midchain radicals, to indicate that they are associated with formation of a long-chain branchpoint. These radicals could undergo scission back to the initial reactants, but this reversibility can be neglected in comparison with macromonomer propagation since $k_{mac}[P^\bullet][U] \gg k_\beta[Q_L^\bullet]$. Similarly, macromonomer addition to the midchain radicals ($Q_n^{ijk\bullet}$), can be reasonably ignored here since $(k_p^t \times k_{mac}/\ k_p \times [Q][U])/(k_{mac} \times [R][U]) = k_p^t[Q]/(k_p[R]) \ll 1$.

Results and Discussion

ST/BA semibatch experiments were run with monomer mass feed ratios of 75/25, 50/50, and 25/75; the free monomer concentration profiles are plotted in Figure 1, and Figure 2 shows the corresponding polymer weight-average molecular weight (M_w) profiles. Homopolymerization of ST[1] and BA[7] under the same reaction conditions are described elsewhere. The low residual monomer concentrations in Figure 1 are characteristic of starved-feed operation, and well represented by model simulations. Note that all of the rate coefficients for propagation and termination,

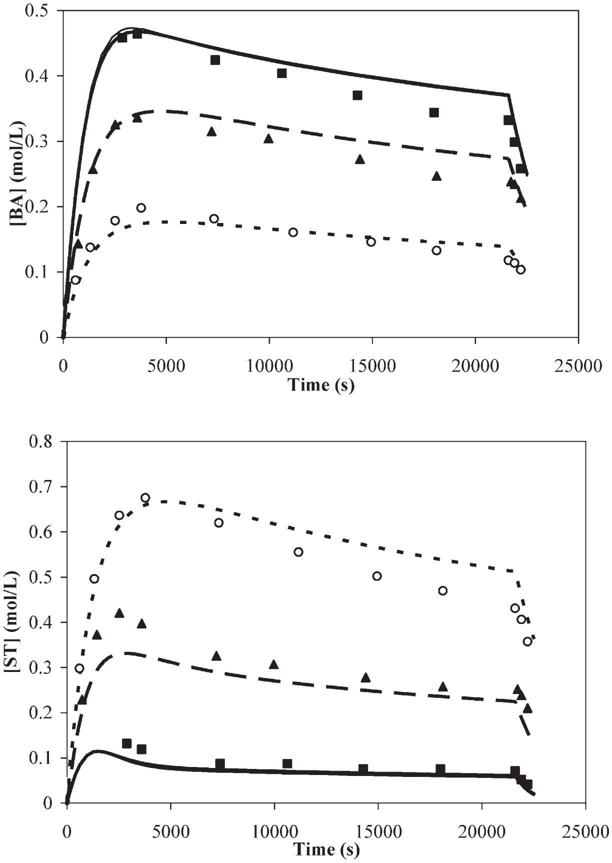


Figure 1.

[BA] (top) and [ST] (bottom) semibatch experimental profiles (points) and model predictions including macromonomer reaction (lines): ST/BA 75/25 copolymerization (○,---); ST/BA 50/50 copolymerization (▲, — —); ST/BA 25/75 copolymerization (■, ——). Lighter lines for ST/BA 25/75 are simulations without macromonomer reaction.

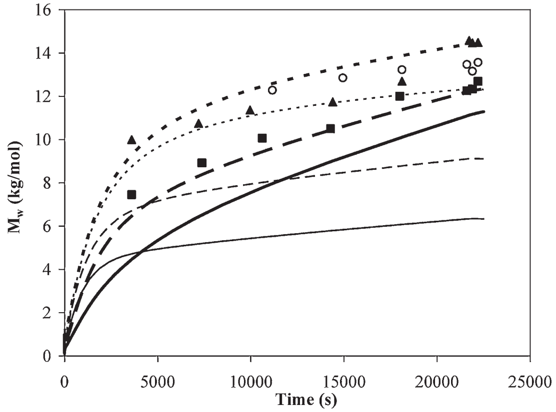


Figure 2.
Experimental polymer weight-average molecular weight (M_w) profiles (points) and model predictions (lines, heavier lines simulated with macromonomer reactions; lighter lines without macromonomer reactions): ST/BA 75/25 copolymerization (○,---); ST/BA 50/50 copolymerization (▲, — —); ST/BA 25/75 copolymerization (■, ——).

including copolymerization penultimate reactions and the reactions involving the formation and reaction of midchain radicals, were taken from literature. The agreement with experimental monomer profiles is an indication that we have achieved a good understanding of this complex copolymerization system. It is also important to note that the predictions of monomer profiles are not sensitive to the macromonomer reactions, as demonstrated in Figure 1 by the comparison of simulations with (heavier lines) and without (lighter lines) macromonomer reactions for the ST/BA 25/75 system; the two curves are difficult to distinguish as they coincide almost exactly.

As shown in Figure 2, M_w values are found to increase with increasing fraction of ST in the system. There is also a general increase in M_w with time for all experiments, with a more significant increase observed for recipes with higher BA fractions. Two sets of simulation results are shown, with and without the reactivity of macromonomer considered. The simulations without macromonomer reactions fail to follow the significant increase in M_w, despite the addition of LCB to the model. It might be possible to match the experimental increase by increasing the LCB rate coefficient, but the required value would be much greater than other current literature estimates.[2i,15] It is only when macromonomer reactivity is considered that the model is able to represent the significant increases in M_w observed experimentally, as shown by the heavier lines in Figure 2.

There is a significant difference in how LCB and macromonomer reactions affect the number of chains in the system: intermolecular chain transfer to polymer does not alter the total number of chains in the system, while macromonomer reaction reduces chain concentration (see Table 1). Thus, it is useful to compare model predictions to the evolution of the complete molecular weight distribution (MWD), as shown in Figure 3 for the ST/BA 25/75 semibatch experiment conducted with 65 wt% final polymer content and monomer feed time of 21600 s. A clear shift of the experimental distributions to higher values is seen with increasing time. This trend is captured by the simulations that include macromonomer reaction, especially the significant shift in higher molecular weight side, as shown in Figure 3b. By only considering LCB, the simulated MWD curves (Figure 3c) cannot capture the significant shift in the distribution. Thus, consideration of the complete MWD

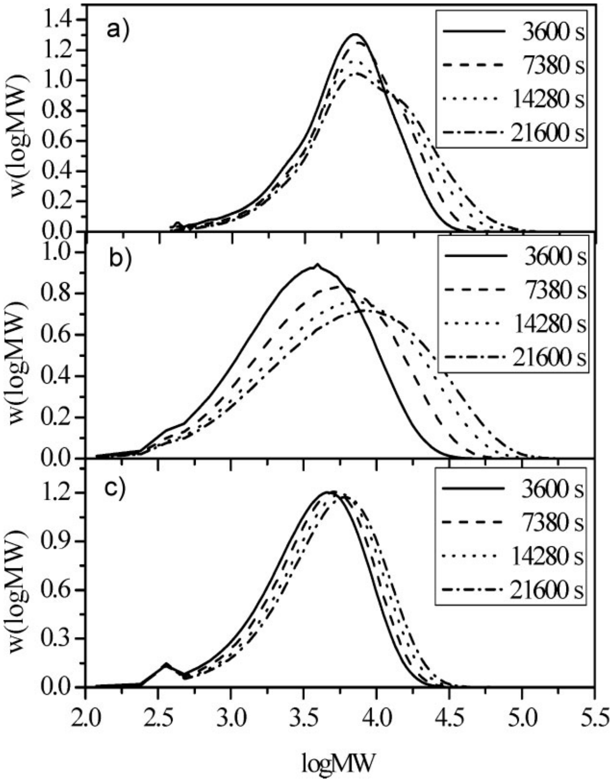


Figure 3.
Experimental (a) and simulated ((b), with macromonomer reaction; (c), without macromonomer reactions) molecular weight distributions with time for ST/BA 25/75 semibatch experiment conducted in xylene at 138 °C with 2 wt% TBPA relative to BA, 65 wt% final polymer content and total monomer feed time of 21600 s.

provides another strong indication of the importance of macromonomer addition reactions in this system.

Conclusions

Semibatch starved-feed free radical solution copolymerizations of styrene (ST) and butyl acrylate (BA) with various monomer compositions were carried out. The significant increase in polymer weight-average molecular weight (M_w), as well as the shift in the entire polymer MWD, is explained by assuming faster β-scission rate of BA midchain radical with an adjacent styrene unit and the propagation of resultant macromonomer. A full mechanistic model for copolymerization of ST and BA has been built in Predici to represent the experimental system. This work will be extended to consider the high temperature terpolymerization of acrylates, methacrylates and styrene.

Acknowledgements: We thank E. I. du Pont de Nemours and Co. and the Natural Sciences and Engineering Research Council of Canada for financial support of this work.

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