# Midchain Transfer to Polymer in Styrene−Poly(butyl acrylate) Systems: Direct Evidence of Retardative Effects

**Stuart C. Thickett and Robert G. Gilbert***

*Key Centre for Polymer Colloids, School of Chemistry F11, Sydney University, NSW 2006, Australia*

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## Introduction

Branching in poly(butyl acrylate) (polyBA) systems is a well-accepted process that occurs via two reactions: a bimolecular reaction, intermolecular chain transfer by hydrogen atom abstraction (long chain branching, LCB), and a unimolecular reaction, intramolecular "backbiting" (short chain branching, SCB). The relative amount of each type of branching depends on the monomer−polymer ratio.[1] $^{13}$C NMR is used to quantify the overall amount of branching, but it is hard to quantify the relative amounts of SCB and LCB. Both result in a radical which is slow to propagate.[2,3] Modeling[4−6] has attempted to account for retardation effects arising from slow propagation from tertiary radical sites formed in the branching process.

These two distinct branching processes cannot be studied separately in BA homopolymerizations. Hence, it is difficult to determine the impact that each has on the overall kinetics. Here we investigate LCB in isolation by seeded emulsion experiments using a polyBA latex in the presence of styrene monomer: in such a system there are no growing polyBA ends, and so SCB cannot occur. Styrene was chosen both because it does not branch and its emulsion polymerization kinetics are well understood.[7−9]

## Experimental Section

**Reagents.** BA and styrene (Aldrich) were purified with an inhibitor removal column (Aldrich) and stored at 4 °C until use, deoxygenated by bubbling high-purity $N_2$ and then degassing under vacuum. Sodium dodecyl sulfate (SDS, Aldrich) and potassium persulfate (KPS, Merck) were used as received.

**Seed Latex Synthesis.** SDS (1.74 g, 3.67 mmol) was dissolved in Milli-Q grade water (409 g). BA (44.06 g, 0.35 mol) was added and stirred vigorously to effect emulsification; the mixture was then heated (80 °C), while high-purity nitrogen was bubbled through the mixture. KPS (0.38 g, 1.46 mmol) dissolved in 5 mL of water was added via a syringe. Polymerization took place for 3 h; the resultant latex was filtered through glass wool and then dialyzed against distilled water for a week with daily changes of water. Particle size measurements (using both a particle size distribution analyzer (Polymer Labs) and capillary hydrodynamic fractionator (Matec)) confirmed a number-average radius of 27 nm and weight: number-average size dispersity as 1.05. The particle number density was $8.5 \times 10^{17}$ L$^{-1}$.

**Chemical Initiation.** Styrene (5 g, 48 mmol), Milli-Q water (17 g), and seed latex (10 g) were separately degassed under vacuum and then loaded into a dilatometer. SDS (0.005 g, 3.5 $\mu$mol) was added, the dilatometer sealed with a rubber septum, and the headspace evacuated via a syringe at room temperature. Magnetic stirring of the solution took place overnight to allow transfer of monomer to the particle interior, and the mixture was then heated to 50 °C. Stirring was ceased and the reaction vessel evacuated again to remove dissolved oxygen.

A KPS solution (1 mL) was added via a syringe; following this a glass capillary (1.51 mm radius) was inserted into the top of the vessel. Water was added until the solution was 10−12 cm up the capillary; stirring then recommenced. Dodecane (1 mL) was added to the top to prevent evaporation. The meniscus height was tracked automatically to provide conversion/time data. Duplicate experiments at five different initiator concentrations (spanning 2 orders of magnitude) were performed.

**$\gamma$-Radiolysis Initiation.** Polymerization was initiated using a $^{60}$Co $\gamma$ source (dose rate = 105 Gy h$^{-1}$). The automated dilatometr was lowered into the radiation source until the polymerization rate reached a steady state and then removed from the source, allowing the rate decrease to be monitored.

## Results and Discussion

**Chemically Initiated Experiments.** The rate in an emulsion polymerization is given by

$$\frac{dx}{dt} = \frac{k_p[M]_p N_p}{n_M^0 N_A}\bar{n} \tag{1}$$

where $x$ is the fractional conversion, $k_p$ the propagation rate coefficient, $[M]_p$ the intraparticle monomer concentration, $n_M^0$ the initial monomer concentration per unit volume of aqueous phase, $N_p$ the particle number per unit volume of aqueous phase, $N_A$ Avogadro's constant, and $\bar{n}$ the average number of radicals per particle. Emulsion polymerizations of styrene in particles of this size obey "zero-one" kinetics (radical entry into a particle already containing a growing radical results in rapid termination). For such systems, chemical and $\gamma$ rate data yield[8] model-free values of the rate coefficients for radical entry into particles ($\rho$) and radical exit/loss from particles ($k$). There are reliable predictive models for entry[7] and exit[10] for this type of styrene system, where it is established[8] that the loss is second-order with respect to $\bar{n}$, as an exited radical reenters another particle irreversibly.

Rate data using chemical initiation (Figure 1) give steady-state $\bar{n}$ values significantly lower than predicted by theory. This would mean that $\rho$ is far lower, and/or that $k$ is far higher, than predicted for styrene in a polystyrene seed, for which the models are reliable. As radical entry depends only on aqueous-phase kinetics, $\rho$ should not be dependent on the particle interior, leaving the radical loss process as the parameter being affected by the presence of polyBA.

**$\gamma$-Relaxation Experiments.** Data analysis of the out-of-source polymerization periods (Figure 2) allowed a value of $k$ to be determined. First- and second-order loss kinetics were fitted to the data; first- and second-order loss kinetics cannot be easily distinguished from rate data.[8]

The first- and second-order loss rate coefficients were $k = (2.2 \pm 1.3) \times 10^{-2}$ and $(4.2 \pm 1.1) \times 10^{-2}$ s$^{-1}$, respectively. These values are both significantly higher than the predicted values for this system ($k = 9 \times 10^{-3}$ s$^{-1}$ using first-order loss, $1 \times 10^{-2}$ s$^{-1}$ for second-order

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* Corresponding author: Fax +61-2-9351 8651; Ph +61 2 9351 3366; e-mail gilbert@chem.usyd.edu.au.

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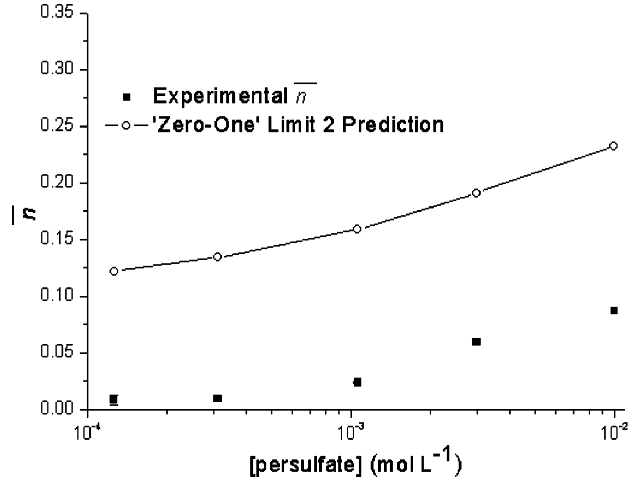


**Figure 1.** Comparison of experimental steady-state values of $\bar{n}$ with those predicted by "limit 2a" kinetics: points, experiment; line, theory.

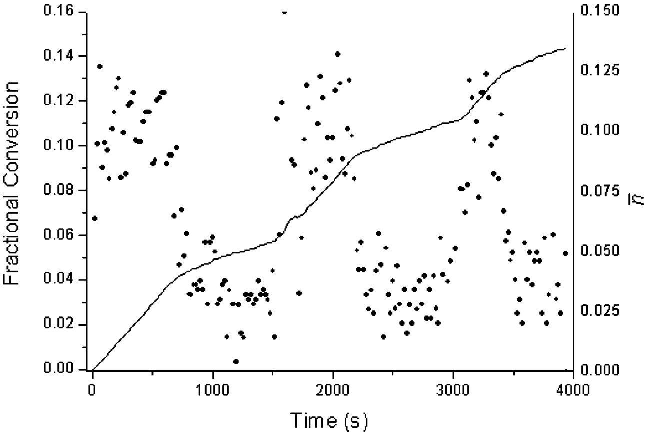


**Figure 2.** Conversion/time data (line) and $\bar{n}$-time (points) data for the $\gamma$-radiation-initiated polymerization of styrene in a polyBA seed latex.

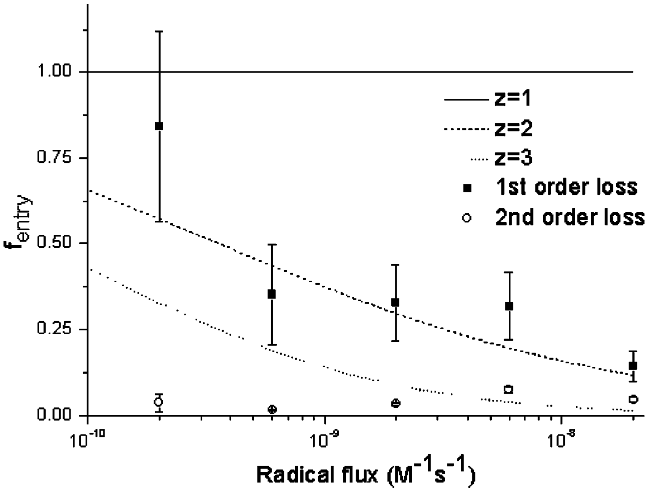


**Figure 3.** $f_{entry}$ vs radical flux for chemically initiated experiments, with the data processed assuming first-order loss (black squares) and second-order loss (open circles). Lines: predicted entry efficiency from the Maxwell–Morrison model, for $z$ (critical degree of polymerization for entry) = 1 (solid line), 2 (dashes), and 3 (dots).

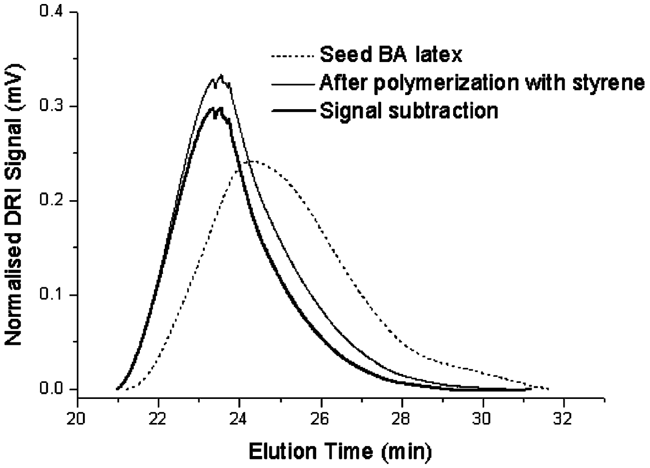
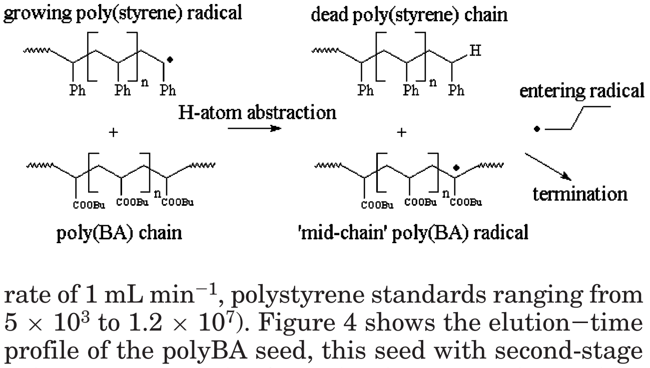


**Figure 4.** SEC elution chromatograms showing poly(butyl acrylate) seed latex (dotted line), sample after second-stage polymerization with styrene (thin solid line), and the formed poly(styrene) determined via weighted signal subtraction (thick solid line).

**Scheme 1. Transfer of Radical Activity from Growing Poly(styrene) Radical to PolyBA Backbone as a Means To Explain Low $\bar{n}$ Values**



loss) and partially explain the significantly reduced steady-state rate.

**Entry Efficiency.** Using our values of $k$ and $\rho$, radical entry efficiency ($f_{entry}$, the fraction of initiator-derived radicals that enter a particle) values were calculated. First-order loss kinetics gives $f_{entry}$ values in accordance with the Maxwell–Morrison "aqueous phase growth" model[7] that predicts the entering species are oligomers of length 2–3 (Figure 3). Similar calculations assuming second-order loss kinetics give $f_{entry}$ values that are substantially lower than predicted by the model, which seems incorrect as a different particle interior should not affect polymerization in the aqueous phase.

An explanation for first-order loss is that transfer to polyBA is the dominant chain-stopping mechanism for growing styrene radicals, with the formed midchain radical unable to desorb from a particle. If propagation from the backbone site is slow, the next entry event will terminate this radical and lead to radical loss (Scheme 1). This seems feasible, given that there is evidence from simulations that propagation off this backbone site is dramatically slower than "conventional" propagation.[11]

The significance of intermolecular chain transfer is shown in the molecular weight distribution (MWD) of formed polymer (performed on a Shimadzu SEC system with 3 × HT6E Waters columns, THF eluent with a flow rate of 1 mL min$^{-1}$, polystyrene standards ranging from $5 \times 10^3$ to $1.2 \times 10^7$). Figure 4 shows the elution–time profile of the polyBA seed, this seed with second-stage polystyrene, and the formed polystyrene obtained by subtracting the suitably normalized[12] MWD of the seed. It is apparent that the formed polystyrene has significantly lower molecular weight than predicted from the well-tested theory for this quantity in a styrene zero-one system[13] (Figure 5). Using the "ln $P$" method[14]

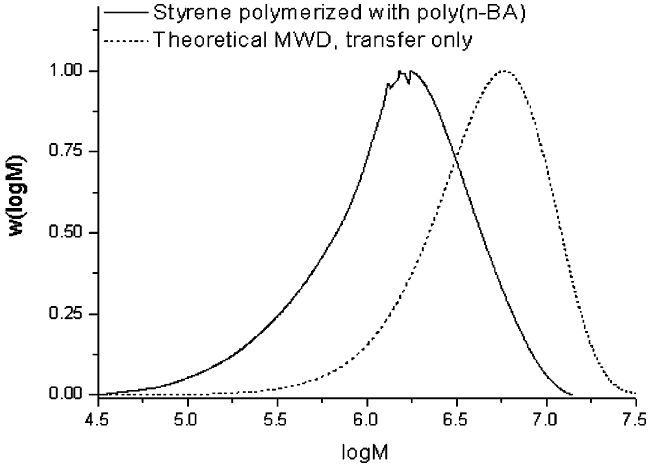


**Figure 5.** SEC distribution of formed poly(styrene) (solid line) from a chemically initiated experiment ([persulfate] = 3 mM) and the predicted GPC distribution (broken line) assuming transfer to monomer is the dominant chain stopping mechanism.

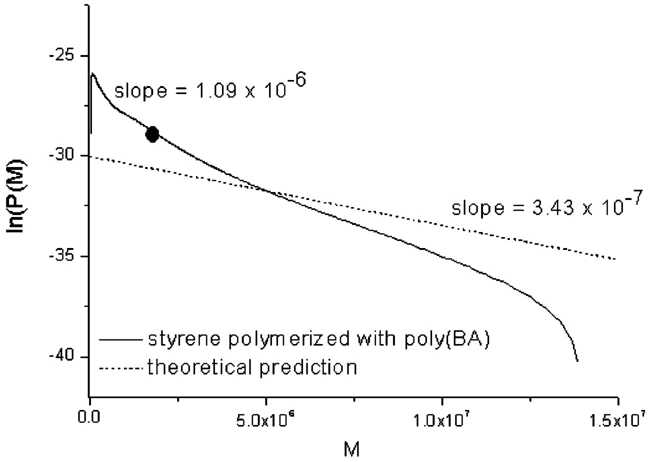


**Figure 6.** Observed and predicted ln $P(M)$ for the formed polystyrene (solid line) MWD of Figure 3. The black circle is at the peak maximum in the original SEC distribution (where the slope is taken from), which corrects for band broadening. The downward curvature of the ln $P$ plot at high molecular weights is due to the sensitivity of the SEC signal subtraction process, to which the slope at the SEC maximum used to find the transfer constant is insensitive.

(plotting the logarithm of the number MWD as a function of molecular weight), including correcting for SEC band broadening,[15,16] the slope of the ln $P$ plot at the maximum in the SEC distribution (Figure 6) is $k_{\mathrm{tr,pol}}[\mathrm{polyBA}]/k_{\mathrm{p}}[\mathrm{styrene}]M_0$, where [polyBA] and [styrene] are polymer and monomer concentrations within the particle respectively, $k_{\mathrm{tr,pol}}$ is the rate coefficient for transfer to polymer, and $M_0$ is the styrene molecular weight. This yields $k_{\mathrm{tr,pol}} = 0.101\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, 10 times higher than that for transfer to monomer.[17] This is a significant effect that is consistent with first-order radical loss by retardative transfer. This value is also over 20 times higher than the estimated value of $k_{\mathrm{tr,pol}}$ found by Plessis et al. by model fitting[18] and may provide further insight into modeling styrene–butyl acrylate copolymerization reactions.

This means of obtaining the rate coefficient for transfer from a polystyryl (or styryl) radical to polyBA provides with a means to study cross-intermolecular chain transfer separately from the BA backbiting reaction. Similarly, the magnitude of the exit rate coefficient in this system compared to that calculated with the reliable model for styrene/polystyrene seeded growth[8] suggests that, on average, one in 20 midchain radicals undergo termination rather than propagation, indicating the slow propagation of styrene off this backbone site.

The data present here are consistent with the hypothesis that a major cause of radical loss (retardation) in this system is transfer from a poly(styryl) radical to polyBA, to form a midchain radical which is slow to propagate and therefore is prone to be terminated.

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