Styrene/*tert*-Butyl Acrylate Random Copolymers Synthesized by Nitroxide-Mediated Polymerization: Effect of Free Nitroxide on Kinetics and Copolymer Composition

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Received July 28, 2007; Revised Manuscript Received October 13, 2007

ABSTRACT: Styrene/*tert*-butyl acrylate (S/*t*-BuA) mixtures were copolymerized using nitroxide-mediated polymerization in bulk at 115 °C using an alkoxyamine unimolecular initiator, 2-[*N*-*tert*-butyl-2,2-(dimethylpropyl)-aminooxy]propionic acid (BlocBuilder) to observe the effect of additional *N*-*tert*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide (SG1) on kinetics and copolymer composition. Polymerizations with 4.5 mol % SG1 relative to BlocBuilder were more controlled with lower polydispersities (from 1.14 to 1.22), and the number-average molecular weight $\bar{M}_n$ exhibited linear behavior with conversion up to ~50%. In contrast, without SG1, apparent rate constants were greater but higher polydispersities were observed, and $\bar{M}_n$ vs conversion deviated from the ideal linear relationship at low conversions ~20%. The value of k_pK (k_p = propagation rate constant, K = equilibrium constant) for *t*-BuA at 115 °C was 3.0×10^{-6} s^{-1} and is lower than other acrylic monomers. The copolymers were richer in *t*-BuA than the feed composition at low initial *t*-BuA feed compositions $f_{t-\text{BuA},0}$ (20 mol %) but became richer in styrene when $f_{t-\text{BuA},0} > 40$ mol %. Copolymer reactivity ratios ranged from $r_{t-\text{BuA}} = 0.09$ to 0.12 and $r_S = 0.40$ to 0.49 using Fineman−Ross, Kelen−Tüdos, and nonlinear least-squares fitting methods.

Introduction

Controlled free radical polymerization chemistry has increased the ease by which well-defined polymers with specific microstructure are made compared to traditional methods such as ionic polymerization.[1−5] The latter method has long been used to produce block copolymers with narrow molecular weight distributions and controlled microstructures.[6,7] Although it approaches the level of control over segment length and microstructure exhibited by ionic polymerization, controlled free radical polymerization differs from ionic polymerization in that it avoids rigorous solvent and monomer purifications, protection of functional groups, and air-free transfer.[6] Further, the use of controlled free radical polymerization opens the way to different monomer combinations and/or sequences that were unattainable via ionic polymerization.

tert-Butyl acrylate (*t*-BuA) homopolymers and block copolymers have been synthesized by several controlled/"living" radical polymerization techniques such as atom transfer radical polymerization (ATRP),[8−11] nitroxide-mediated radical polymerization (NMP),[12−15] and reversible addition−fragmentation chain transfer polymerization (RAFT).[16−19] Incorporation of *t*-BuA into polymer segments is desirable due to its facile cleavage to yield acrylic acid functional groups,[8,9] and characterization of *t*-BuA-containing copolymers with other organo-soluble monomers may in some cases be easier than feed mixtures of acrylic acid/organo-soluble monomers. Furthermore, heat transfer issues of directly polymerizing acrylic acid in concentrated solutions may be problematic.[20,21] In previous studies, attention has been largely devoted to synthesizing pure segments of poly(*t*-BuA) sequentially in segmented block copolymers. For many applications, having the *t*-BuA units tapered or randomly located along a segment is desirable. Tapering may be more practical in scaling-up processes for block copolymer production by controlled radical polymerization to avoid an intermediate step to cross over to a second block. We desire to copolymerize *t*-BuA to impart functionality into styrenic blocks. Surprisingly, data are extremely sparse regarding *t*-BuA copolymerization with styrene[22,23] although data regarding other acrylic monomers copolymerized with styrene are abundant in conventional free radical copolymerization[24,25] and even in controlled radical polymerization.[26−31] The focus of the following study was strictly geared toward NMP to avoid potential catalyst issues associated with ATRP and to avoid the synthesis of chain transfer agents required for RAFT that are not currently commercially available.

Traditionally, the limitation of NMP, when using 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) free radical as a mediator (which was one of the first nitroxides to produce pseudo-"living" polymers), was the selection of the monomer which had to be styrenic-based such as styrene,[1,2] vinylpyridine,[32−34] and other similarly substituted styrenics.[35−37] When trying to polymerize other monomers such as acrylics like *t*-BuA with the aid of TEMPO as a mediator, such polymerizations were limited to compositions requiring styrene as a comonomer as well as temperatures reaching 125 °C or higher.[26] A great deal of effort was spent on the development of a mediator that can operate at lower temperatures and for a wider range of monomers or comonomers. Nitroxides such as 2-benzolyoxy-1-phenylethyl-di-*tert*-butyl nitroxide (BS-DBN) with higher homolysis rates were able to polymerize *t*-BuA at lower temperatures than that used by TEMPO-mediated systems (120 °C) in a controlled manner.[12] More recently, acyclic *β*-phosphonylated nitroxides such as *N*-*tert*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide, also known as SG1 (Figure 1a), were developed to polymerize systems much faster than TEMPO-mediated

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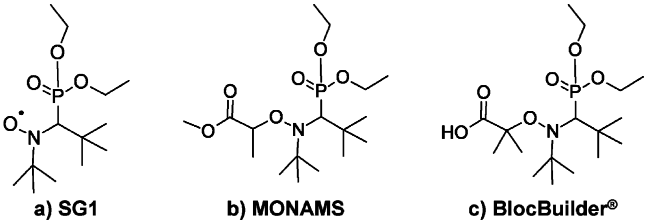

Figure 1. Structures of various alkoxyamine mediators and unimolecular initiators for controlled radical polymerization: (a) *N-tert*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide (SG1), (b) *N-tert*-butyl-*N*-1-diethylphosphono-2,2-dimethylpropyl-*O*-1-methoxycarbonylethylhydroxylamine (MONAMS), and (c) 2-[*N-tert*-butyl-2,2-(dimethylpropyl)aminooxy]propionic acid (BlocBuilder).

systems using temperatures as low as 90 °C.[38,39] The SG1-mediated systems have recently been adapted for the polymerization of *t*-BuA[14,15] and other acrylic-based monomers such as *n*-butyl acrylate,[40−43] dimethylacrylamide,[44−46] hydroxyethyl acrylate,[47] and acrylic acid.[20,48,49] Polymerization of methyl methacrylate and methacrylic acid using SG1 mediators has also recently been reported.[50−52] For *n*-BuA initiated by *N-tert*-butyl-*N*-(1-diethylphospho-2,2-dimethypropyl)-*N*-aminooxystyrene (styryl-DEPN), Lacroix-Desmazes et al. concluded that the addition of 5 mol % SG1 with respect to the alkoxyamine initiator improved the control of the polymerization rate and more pseudo-“living” behavior as exhibited by a linear increase in molecular weight with conversion.[40] A styryl-DEPN initiator with a 66% excess of SG1 also polymerized dimethylacrylamide with polydispersities ranging from 1.07 to 1.20 and molecular weights up to nearly 50 kg/mol in bulk.[44] Couvreur et al. used the organo-soluble SG1-based unimolecular initiator *N-tert*-butyl-*N*-1-diethylphosphono-2,2-dimethylpropyl-*O*-1-methoxycarbonylethylhydroxylamine known as MONAMS (Figure 1b) with a 9 mol % excess of free nitroxide SG1 relative to MONAMS to polymerize pure acrylic acid in 21 wt % 1,4-dioxane solution at 120 °C with polydispersities ranging from 1.3 to 1.5 and molecular weights up to about 15 kg/mol.[20] Laruelle et al. polymerized styrene in bulk using SG1/MONAMS = 5 mol % at 120 °C with low molecular weights up to ~2 kg/mol and polydispersity index equal to 1.25 which was subsequently used to initiate a poly(acrylic acid) block.[49] Bian and Cunningham found a ratio of SG1/MONAMS = 6−12 mol % was effective in controlling the polymerization of hydroxylethyl acrylate with polydispersities less than 1.3 and molecular weights up to 90 kg/mol in bulk and in aqueous solution.[47]

More recently, other SG1-based alkoxyamines have been developed such as the isobutyric acid-functionalized SG1 which is 2-[*N-tert*-butyl-2,2-(dimethylpropyl)aminooxy]propionic acid, also known as BlocBuilder, which is available from Arkema[39,51,53−57] (Figure 1c). BlocBuilder is particularly attractive due to its water solubility when neutralized and its carboxylic acid functional group which may be useful for emulsification, blend compatibilization, and block copolymer formation. BlocBuilder has thus far been used in bulk,[51,53,55] solution,[30,45,46,54] and miniemulsion polymerizations.[55−57] In bulk using BlocBuilder, *n*-butyl acrylate and styrene have been polymerized with molecular weights ~20 kg/mol and polydispersities ranging from 1.12 to 1.40,[53,55] and methyl methacrylate/styrene mixtures were polymerized with 10% molar excess of SG1 to give polymers with molecular weights up to 24 kg/mol with polydispersities ranging from 1.21 to 1.42.[51] However, the ability of BlocBuilder/SG1 systems to control polymerizations of *t*-BuA has not been widely studied.[15] The versatility of BlocBuilder thus warrants further examination, particularly when coupled to the *t*-BuA/styrene which is of interest in this paper. We thus seek to determine whether BlocBuilder or a BlocBuilder/SG1 mixed mediator system is more effective at controlling the copolymerization of *t*-BuA/styrene in bulk and to determine the effects on the final copolymer composition. The results of this study will be useful for developing procedures to produce well-defined tapered or segmented blocks with *t*-BuA functionality for ultimate application in separations media,[58,59] catalyst supports,[60] and nanoreactors.[61]

Experimental Section

Materials. Styrene (99%), *tert*-butyl acrylate (*t*-BuA) (98%), basic alumina (Brockmann, Type 1, 150 mesh), and calcium hydride (90−95% reagent grade) were purchased from Aldrich. Methanol (99.8%) and methylene chloride (99.5%) were obtained from Fisher. The styrene and *tert*-butyl acrylate monomers were both purified by passing through a column of basic alumina mixed with 5 wt % calcium hydride and were stored in a sealed flask under a head of nitrogen in a refrigerator until needed. 2-[*N-tert*-Butyl-2,2-(dimethylpropyl)aminooxy]propionic acid, also known as BlocBuilder (99%), was purchased from Arkema and was used without further purification. *N-tert*-Butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide, also known as SG1 (>85%), was kindly donated by Noah Macy of Arkema and used as received.

Synthesis of *tert*-Butyl Acrylate/Styrene Random Copolymers. The syntheses were all performed in a 100 mL three-neck round-bottom glass flask equipped with a condenser, thermal well, and a magnetic Teflon stir bar. The flask was placed inside a heating mantle, and the equipment was placed on a magnetic stirrer. A specific formulation for an initial feed composition of *t*-BuA ($f_{t-\mathrm{BuA},0}$) equal to 40 mol % is given as an example. In all cases, the target molecular weight was ~45 kg/mol and was calculated by the mass of monomers relative to the moles of BlocBuilder initiator. BlocBuilder (0.3 g, 0.79 mmol) and SG1 (0.01 g, 0.034 mmol, 4.5 mol % relative to BlocBuilder) were added to the flask with the stirrer which was then sealed with a rubber septum. A thermocouple was inserted into the temperature well and connected to a controller. A condenser was connected to one of the necks and capped with a rubber septum which had a needle placed to relieve the pressure of the nitrogen purge that was applied during the entire course of the reaction. The condenser was connected to a chilling unit (Neslab 740) which used a glycol/water mixture to condense any vapors produced during the experiment and thus prevent loss of the monomers due to evaporation. The previously purified *t*-BuA (16.23 g, 0.127 mol) and styrene (19.66 g, 0.189 mol) were injected into the system using disposable 5 mL syringes to be able to accurately obtain the required feed compositions. Once stirring was started and the chilling unit was set to 5 °C, an ultrapure nitrogen flow was introduced to purge the system during monomer injection, as well as 15 min postinjection, at room temperature. The reactor was then heated to 115 °C at a rate of about 10 °C/min while maintaining a nitrogen purge. The time when the reactor reached 115 °C was taken as the start of the reaction ($t = 0$). Samples were taken with a syringe periodically until the samples became too viscous to withdraw. For the specific example cited, the polymerization time was 109 min. For the experiments with low $f_{t-\mathrm{BuA},0}$, samples were precipitated in methanol, and for the experiments with a high $f_{t-\mathrm{BuA},0}$, samples were precipitated in a 50% v/v (distilled water/methanol) mixture. The samples were left to settle for several hours, then decanted, and dried overnight in a vacuum oven at 70 °C for samples with low $f_{t-\mathrm{BuA},0}$ and 90 °C for samples with high $f_{t-\mathrm{BuA},0}$, to remove any solvent or unreacted monomer. The higher temperature for samples with high $f_{t-\mathrm{BuA},0}$ was used to facilitate remove of the water used to precipitate the polymers. The final yield for the particular synthesis given was 15.07 g (42% conversion) with number-average molecular weight M_n = 19.3 kg/mol, weight-average molecular weight M_w = 22.2 kg/mol, and polydispersity index = M_w/M_n = 1.15 determined by gel permeation chromatography calibrated with linear poly(styrene) standards. The composition of the copolymer was 37 mol % *t*-BuA

Table 1. Summary of *tert*-Butyl Acrylate/Styrene Copolymerizations Performed in Bulk at 115 °C

$f_{t\text{-BuA},0}$[a]	r[b]	time (min)	% conversion[c]	$F_{t\text{-BuA}}$[d]	M_w (kg/mol)[e]	M_n (kg/mol)[e]	M_w/M_n[e]
0	0	50	63		21.5	17.5	1.23
0	0.045	96	31		24.4	20.5	1.19
23	0	42	43	32	6.0	4.7	1.28
20	0.045	90	45	31	21.0	18.6	1.14
41	0	60	33	41	8.6	7.9	1.27
40	0.045	109	42	37	22.2	19.3	1.15
60	0	76	48	47	22.7	17.9	1.27
60	0.045	141	38	48	23.0	19.6	1.18
79	0	111	39	56	16.4	12.3	1.22
81	0.045	125	42	63	24.7	21.0	1.18
100	0	212	66		15.2	13.4	1.23
100	0.045	128	46		26.7	22.1	1.22

[a] Initial % molar feed composition of *tert*-butyl acrylate. [b] $r = [\text{SG1}]_0/[\text{ BlocBuilder}]_0$. [c] Conversion determined gravimetrically. [d] Final copolymer % molar composition ($F_{t\text{-BuA}}$) determined by Fourier transform infrared spectroscopy. [e] Number-average (M_n), weight-average (M_w) molecular weight, and polydispersity index (M_w/M_n) determined by gel permeation chromatography relative to poly(styrene) standards in tetrahydrofuran.

using nuclear magnetic resonance (NMR) and Fourier transform infrared spectroscopy (FT-IR).

Synthesis of *tert*-Butyl Acrylate/Styrene Random Copolymers for Determination of Reactivity Ratios. To determine the copolymer reactivity ratios, polymerizations were conducted identically to those in the preceding section except that the polymerization times were kept to 15 min. This was to ensure a low conversion and thus avoid any corrections for compositional drift. In each case, the ratio of SG1 to BlocBuilder was 4.5 mol %. The time at which the solution reached 115 °C was taken as the start of the reaction ($t = 0$). For each composition, three samples were taken over a short time span (typically at polymerization times of 5, 10, and 15 min) such that the conversion for each composition would be nearly identical and to estimate an error for the measurement. For the reactions with a low $f_{t\text{-BuA}} < 40\%$, the samples were precipitated in methanol, and those with a higher $f_{t\text{-BuA}}$ were precipitated in a 50/50 v/v distilled water/methanol mixture. The samples were left to settle for several hours and were then dried overnight in a vacuum oven at 70 °C for samples with low $f_{t\text{-BuA}}$ and 90 °C for samples with high $f_{t\text{-BuA}}$ to remove any precipitating solution or unreacted monomer.

Characterization. The overall monomer conversion was determined by gravimetry done on the dry samples until constant weight was attained as indicated in the previous section. The molecular weight distribution was measured using gel permeation chromatography (GPC, Water Breeze) which used tetrahydrofuran (THF) as the mobile phase. As mentioned earlier, the copolymers were soluble in organic solvents and therefore did not need further treatment prior to GPC analysis. A mobile phase flow rate of 0.3 mL min^{-1} was applied, and the GPC was equipped with three Waters Styragel HR columns (HR1 with molecular weight measurement range of $10^2-5 \times 10^3$ g/mol, HR2 with molecular weight measurement range of $5 \times 10^2-2 \times 10^4$ g/mol, and HR4 with molecular weight measurement range $5 \times 10^3-6 \times 10^5$ g/mol) and a guard column was used. The columns were heated to 40 °C during the analysis. The molecular weights were determined by calibration with narrow molecular weight distribution poly(styrene) standards. The GPC was equipped with both ultraviolet (UV 2487) and differential refractive index (RI 2410) detectors. The UV detector was set to a wavelength of 255 nm to detect the aromatic rings in the poly(styrene)-containing copolymers. Fourier transform infrared spectroscopy (FT-IR) (Spectrum BX, Perkin-Elmer) was used to determine the composition of *t*-BuA in the copolymer by using the carbonyl peak at 1720 cm^{-1} as a marker for the concentration of *t*-BuA in the copolymer while the peak at 700 cm^{-1} was used as the marker for the concentration of styrene in copolymer. ^{1}H nuclear magnetic resonance (NMR) was performed on a copolymer sample to estimate the copolymer composition and thus to provide a calibration standard for the subsequent FT-IR measurements. The ^{1}H NMR measurements were done with a 200 MHz Varian Gemini 2000 spectrometer using deuterated chloroform (Cambridge Isotope Laboratories Inc.) as the solvent in 5 mm Up NMR tubes. After injecting and shimming, the sample was scanned 32 times. The sample used had a feed composition of 60 mol % *t*-BuA, employed 4.5 mol % SG1 relative to BlocBuilder, and was polymerized for 15 min, leading to a conversion of 11%. The copolymer composition was 43 mol % *t*-BuA using the resonances due to the aromatic protons corresponding to the styrene monomers at $\delta = 6.8-7.1$ ppm and the resonances corresponding to the aliphatic backbone and the *tert*-butyl groups from $\delta = 1.5-2.5$ ppm. The molecular weight characteristics for the FT-IR standard copolymer were $M_n = 7.5$ kg/mol, $M_w = 9.7$ kg/mol, and $M_w/M_n = 1.28$ using GPC analysis as described earlier.

Results and Discussion

Styrene-*random*-*tert*-Butyl Acrylate Copolymerization: Effect of SG1 Free Nitroxide on Kinetics. Two different sets of experiments were conducted with the same target molecular weight of 45 kg/mol in bulk that were polymerized at 115 °C. Table 1 summarizes the experiments performed in addition to characterization data for copolymer composition and molecular weight distribution. One set of experiments used BlocBuilder as the unimolecular initiator and the other used BlocBuilder in addition to 4.5 mol % free SG1 nitroxide relative to BlocBuilder. It was previously shown for acrylic acid/styrene copolymerization[29] and *n*-butyl acrylate homopolymerization[40] by nitroxide-mediated polymerization that a proportion of 4.5 mol % of SG1 free nitroxide with respect to MONAMS mediator will exhibit favorable pseudo-“living” character and low polydispersities. We thus used the same relative concentration of SG1 free nitroxide to that of the BlocBuilder initiator in our study. Both sets of experiments were done using the same initial feed compositions of *t*-BuA and styrene in order to be able to draw better comparisons. The various initial molar feed concentrations of *t*-BuA are denoted by $f_{t\text{-BuA},0}$ ($f_{t\text{-BuA},0} = 0\%$, 20%, 40%, 60%, 80%, and 100% were used for our experiments).

Figure 2a shows the first-order kinetic plot of $\ln[(1 - X)^{-1}]$ ($X =$ conversion) vs time for several polymerizations at various $f_{t\text{-BuA},0}$ without free SG1 nitroxide, whereas Figure 2b shows the polymerizations at various $f_{t\text{-BA},0}$ with 4.5 mol % free SG1 nitroxide. When comparing the $\ln[(1 - X)^{-1}]$ vs polymerization time plots, it is apparent that the set of experiments without SG1 free nitroxide have a noticeably greater rate of polymerization than those using free nitroxide as indicated by the slopes derived from the linear fit of the $\ln[(1 - X)^{-1}]$ plot vs time. The slopes of the plots give the apparent rate constants $k_p[\text{P}^\bullet]$, where k_p is the propagation rate constant and $[\text{P}^\bullet]$ is the concentration of propagating radicals. The slopes were taken only in the linear region of the plot where $[\text{P}^\bullet]$ should be constant, typically from data taken in the first 20−25 min of the polymerization. The $k_p[\text{P}^\bullet]$ determined from the plots is slightly larger without the free nitroxide, as summarized in Table

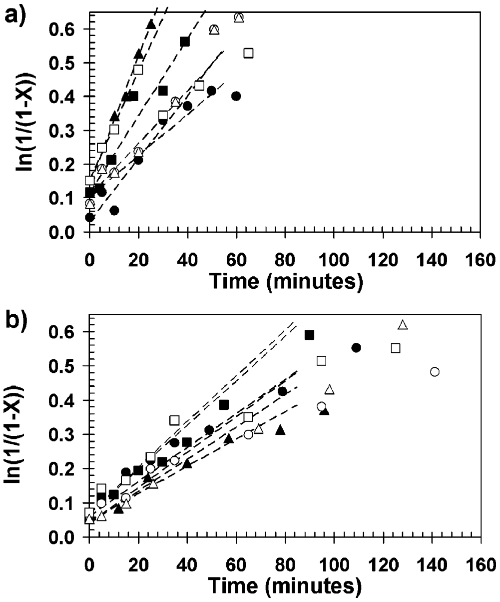

Figure 2. Semilogarithmic plot of $\ln((1 - X)^{-1})$ (where X = conversion) vs time for various styrene/*tert*-butyl acrylate (S/*t*-BuA) compositions polymerized at 115 °C in bulk with (a) no free nitroxide using BlocBuilder as the initiator and (b) 4.5 mol % SG1 free nitroxide relative to BlocBuilder. The various initial molar feed concentrations of *t*-BuA are denoted by $f_{t\text{-BuA},0}$ and are represented symbolically as follows: $f_{t\text{-BuA},0} = 0\%$ (▲), $f_{t\text{-BuA},0} = 20\%$ (■), $f_{t\text{-BuA},0} = 40\%$ (●), $f_{t\text{-BuA},0} = 60\%$ (○), $f_{t\text{-BuA},0} = 80\%$ (□), and $f_{t\text{-BuA},0} = 100\%$ (△). Note that some polymer was formed at the arbitrary initial time in both (a) and (b). This indicates that polymerization was occurring at lower temperatures as is possible when using such alkoxyamines. Polymerizations can occur for such systems as low as 90 °C for styrene and *n*-butyl acrylate.[41]

Table 2. Kinetic Parameters for BlocBuilder/SG1 Nitroxide-Mediated Copolymerization of Styrene with *tert*-Butyl Acrylate in Bulk at 115 °C

without free SG1 nitroxide		with free SG1 nitroxide ($r = 0.045$)[b]		
$f_{t\text{-BuA},0}$[a]	$k_p[P^\bullet]$ ($\times 10^4$ s^{-1})[c]	$f_{t\text{-BuA},0}$	$k_p[P^\bullet]$ ($\times 10^4$ s^{-1})	k_pK ($\times 10^4$ s^{-1})
0	3.2 ± 0.3	0	0.9 ± 0.2	0.039 ± 0.007
23	1.9 ± 0.4	20	1.1 ± 0.2	0.049 ± 0.007
41	1.6 ± 0.3	40	1.1 ± 0.2	0.050 ± 0.007
60	1.3 ± 0.2	60	0.8 ± 0.2	0.038 ± 0.008
79	2.7 ± 0.2	81	1.0 ± 0.2	0.044 ± 0.008
100	2.8 ± 1.0	100	0.7 ± 0.1	0.030 ± 0.003

[a] $f_{t\text{-BuA},0}$ = % molar fraction of *t*-BuA initially in the monomer feed. [b] $r = [\text{SG1}]_0/[\text{BlocBuilder}]_0 = 0.045$. [c] $k_p[P^\bullet]$ obtained from initial slopes of $\ln[(1 - X)^{-1}]$ vs time plots given in Figure 2. Error bars are derived from standard error in slope estimation.

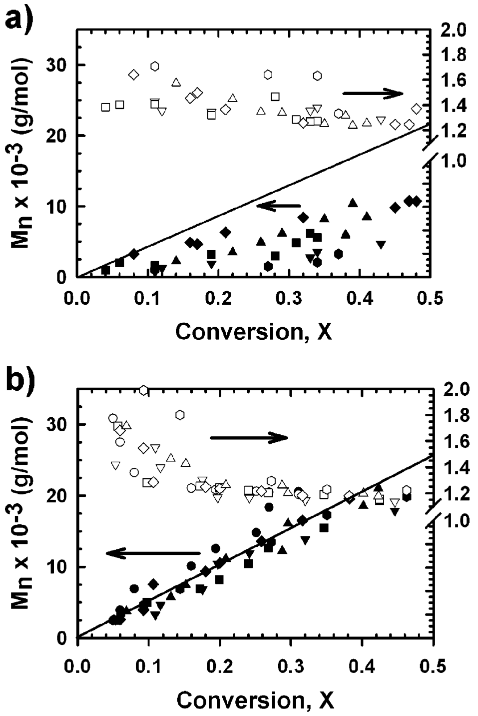

Figure 3. Number-average molecular weight ($\bar{M}_n$) vs conversion X for styrene (S)/*tert*-butyl acrylate (*t*-BuA) mixtures copolymerized in bulk at various initial feed concentrations of *t*-BuA at 115 °C using (a) BlocBuilder only as the initiator and (b) 4.5 mol % SG1 free nitroxide relative to BlocBuilder. The various initial molar feed compositions $f_{t\text{-BuA},0}$ are represented symbolically as follows: $f_{t\text{-BuA},0} = 0\%$ (●), $f_{t\text{-BuA},0} = 20\%$ (▼), $f_{t\text{-BuA},0} = 40\%$ (■), $f_{t\text{-BuA},0} = 60\%$ (◆), $f_{t\text{-BuA},0} = 80\%$ (▲), and $f_{t\text{-BuA},0} = 100\%$ (⬢). Filled symbols denote $\bar{M}_n$ vs X data while open symbols represent the polydispersity index vs X data.

2. The effect of the feed composition in the absence of free nitroxide (Figure 2a) indicates a fairly wide dispersion with no apparent influence of feed composition on $k_p[P^\bullet]$. Note that $k_p[P^\bullet]$ is not significantly different within experimental error for the poly(styrene) and poly(*tert*-butyl acrylate) homopolymerizations with or without added free nitroxide (Table 2). Figure 2b shows that the addition of SG1 free nitroxide results in little change in the apparent rate as a function of feed composition, and the spread of $k_p[P^\bullet]$ values is not as wide as for the case without SG1. More kinetic information can be obtained from the set of experiments with additional free nitroxide, particularly that of the equilibrium between dormant and propagating species that is crucial for the controlled radical polymerization process. The product k_pK was evaluated where K is the equilibrium constant between dormant and propagating radicals.

K has been defined previously as the ratio of the product between the concentration of propagating radicals $[P^\bullet]$ and free nitroxide [SG1] to the concentration of the dormant species [P−SG1]:[20,40,47]

$$K = \frac{[P^\bullet][\text{SG1}]}{[P{-}\text{SG1}]} \tag{1}$$

Because of the large concentration of initial free SG1 used, we assumed $[\text{SG1}] \approx [\text{SG1}]_0$. The chain concentration can be considered to be constant and equal to the initial alkoxyamine concentration; therefore, we can state $[P{-}\text{SG1}] = [\text{BlocBuilder}]_0$. Figure 3b indicates a linear increase in number-average molar mass with monomer conversion over a fairly wide range, which suggests the system follows a controlled behavior and therefore these assumptions are justified. Obviously, direct electron spin resonance (ESR) measurements would have provided useful additional support for this assumption. When combining these assumptions with eq 1, the following equation was revealed.

$$k_pK = k_p\frac{[\text{SG1}]_0[P^\bullet]}{[\text{MAMA}]_0} = r[P^\bullet]k_p \tag{2}$$

The parameter r is the ratio $[\text{SG1}]_0/[\text{BlocBuilder}]_0$. Thus, from the linear region of the kinetic plots, the $k_p[P^\bullet]$ was obtained that, when combined with r (in this case given by 4.5 mol % SG1 relative to BlocBuilder), provides the product k_pK, which is listed in Table 2.

The values obtained in Table 2 can be compared to other polymerizations from literature sources. For the styrene homopolymerization performed at 115 °C, we found $k_pK = (3.9 \pm 0.7) \times 10^{-6}$ s^{-1}. Benoit et al. reported $k_pK = 4.8 \times 10^{-6}$ s^{-1}

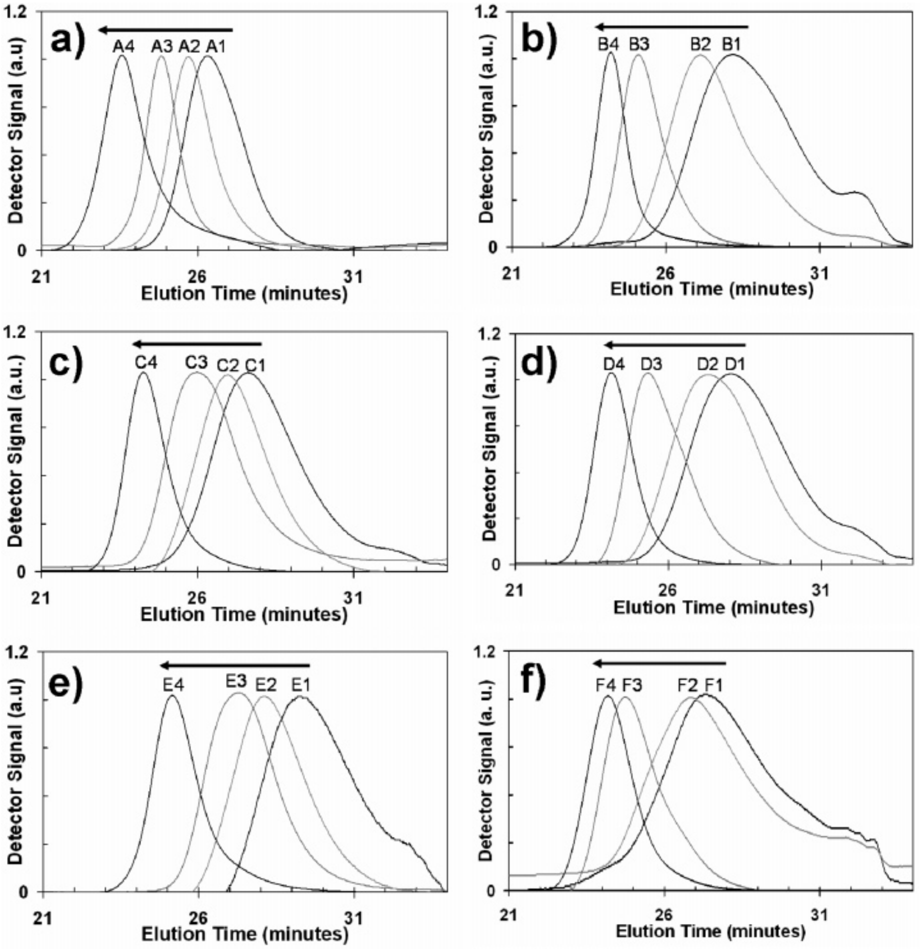

Figure 4. Normalized gel permeation chromatograms of samples taken at various times for styrene/*tert*-butyl acrylate (S/*t*-BuA) copolymerizations performed at 115 °C in bulk with different initial monomer feed concentrations (initial molar feed concentration of *t*-BuA is given by $f_{t-\mathrm{BuA},0}$) and using BlocBuilder or SG1/ BlocBuilder initiator/mediators: (a) without SG1 and $f_{t-\mathrm{BuA},0} = 0\%$; (b) with 4.5 mol % SG1 and $f_{t-\mathrm{BuA},0} = 0\%$; (c) without SG1 and $f_{t-\mathrm{BuA},0} = 60\%$; (d) with 4.5 mol % SG1 and $f_{t-\mathrm{BuA},0} = 60\%$; (e) without SG1 and $f_{t-\mathrm{BuA},0} = 100\%$; (f) with 4.5 mol % SG1 and $f_{t-\mathrm{BuA},0} = 100\%$. Molecular weight data for the samples are summarized in Table 3.

for styrene at 120 °C.[41] These values are in relatively good agreement despite the difference in polymerization temperatures. Using the value for k_p determined using the pulsed-laser photoinitiated polymerization (PLP) technique,[62] the difference in k_p between 115 and 120 °C is about 10%. We evaluated k_pK at 120 °C for styrene elsewhere[21] and found $k_pK = 4.9 \times 10^{-6}$ s^{-1}, so our k_pK value at 115 °C is reasonable. For *t*-BuA homopolymerization with free SG1 nitroxide at 115 °C, we obtained $k_pK = (3.0 \pm 0.3) \times 10^{-6}$ s^{-1}, which is not too dissimilar from that of styrene at 115 °C. We can compare the value obtained to *t*-BuA homopolymerizations performed at 110 °C in a parallel synthesizer with various free nitroxide concentrations.[15] Estimating k_pK from the reported $k_p[\mathrm{P}^\bullet]$ and r of the latter study gave $k_pK = 4.3 \times 10^{-7}$ to 1.0×10^{-6} s^{-1}. Compared to k_pK values for other acrylates such as *n*-butyl acrylate ($k_pK(120\ °\mathrm{C}) = 1.8 \times 10^{-5}$ s^{-1}),[41] acrylic acid ($k_pK(120\ °\mathrm{C}) = 1.1 \times 10^{-5}-1.8 \times 10^{-5}$ s^{-1}),[20] and hydroxyethyl acrylate ($k_pK(120\ °\mathrm{C}) = 2.6 \times 10^{-5}$ s^{-1}),[47] k_pK for *t*-BuA is much lower. Estimation of k_p for *t*-BuA at 115 °C from PLP experiments[63] gives 5.5×10^4 L mol^{-1} s^{-1}, which is more than an order of magnitude higher than that of styrene ($k_{p,\mathrm{styrene}}(115\ °\mathrm{C}) \approx 1.8 \times 10^3$ L mol^{-1} s^{-1})[62] but lower than that of *n*-butyl acrylate ($k_p(120\ °\mathrm{C}) = 8.4 \times 10^4$ L mol^{-1} s^{-1})[41] and acrylic acid ($k_p(120\ °\mathrm{C}) = 1 \times 10^5$ L mol^{-1} s^{-1}).[64] Consequently, K for *t*-BuA at 115 °C = 4.6×10^{-11} mol/L, which is lower than that estimated for styrene based on our data $K_{\mathrm{styrene}}(115\ °\mathrm{C}) = 2.2 \times 10^{-9}$ mol/L and close to that expected for *n*-butyl acrylate and acrylic acid at 120 °C ($K \sim 10^{-10}$ mol/L). Thus, the behavior of *t*-BuA falls between that of styrene and the other acrylates cited. It has a higher propagation rate constant compared to styrene but just slightly below that of the other acrylates. Comparing to acrylic acid, which has a very high k_p and low K, problems associated with highly exothermic conditions due to the high k_p are apparently avoided for *t*-BuA at the conditions used here, and the homopolymerization and copolymerization with styrene proceeded smoothly in bulk.

Styrene-*random-tert*-Butyl Acrylate Copolymerization: Effect of SG1 Free Nitroxide on Molecular Weight Distribution and Control of Polymerization. Figure 3 compares the effect of added SG1 free nitroxide on the control of the polymerization. Without any free nitroxide as indicated in Figure 3a, regardless of feed composition, the number-average molecular weight $\bar{M}_n$ vs conversion plots start to flatten at relatively low conversions and deviate from the theoretical linear behavior expected of a controlled polymerization. The polydispersity indices (PDI) did not vary greatly, typically being approximately 1.3−1.4 regardless of composition or conversion. With 4.5 mol % added SG1 free nitroxide as indicated in Figure 3b, the behavior is markedly different compared to that without free nitroxide. The polymerizations are very close to the theoretical behavior expected up to relatively high conversions (~50%). There is also less variability in $\bar{M}_n$ compared to the case without added SG1. There be some discrepancy in the molecular weights since they were measured relative to poly(styrene) standards, and the copolymers

Table 3. Molecular Weight Distribution Data Corresponding to Samples at Different Polymerization Times Shown in Figure 4

$f_{t-\mathrm{BuA},0}$[a]	r[b]	ID[c]	time (min)	% conversion	M_w[d] (kg/mol)	M_n[d] (kg/mol)	M_w/M_n[d]
0	0	A1	10	29	6.8	5.2	1.29
		A2	20	41	8.9	7.2	1.24
		A3	40	58	13.0	10.7	1.23
		A4	60	63	21.7	17.6	1.23
0	0.045	B1	0	5	4.2	2.4	1.77
		B2	5	6	6.2	3.9	1.59
		B3	40	19	15.3	12.5	1.22
		B4	103	31	25.3	18.9	1.19
60	0	C1	0	8	5.3	3.2	1.64
		C2	5	17	6.9	4.6	1.50
		C3	35	32	10.6	8.4	1.23
		C4	76	48	22.7	17.8	1.27
60	0.045	D1	0	6	4.4	2.6	1.68
		D2	5	9	6.1	4.0	1.55
		D3	35	20	13.0	10.6	1.24
		D4	155	38	25.3	22.2	1.14
100	0	E1	6	27	2.4	1.5	1.64
		E2	37	37	4.3	3.3	1.33
		E3	74	82	6.4	5.3	1.26
		E4	212	66	15.2	12.3	1.23
100	0.045	F1	0	5	6.1	2.6	2.38
		F2	5	6	7.1	3.4	2.08
		F3	69	27	19.4	13.5	1.29
		F4	134	46	26.7	22.1	1.22

[a] $f_{t-\mathrm{BuA},0}$ = initial molar fraction of *tert*-butyl acrylate in the feed. [b] $r = [\mathrm{SG1}]_0/[\mathrm{BlocBuilder}]_0$. [c] ID = identification of peaks labeled in Figure 4. [d] Number-average (M_n) and weight-average (M_w) molecular weight and polydispersity index (M_w/M_n) determined by gel permeation chromatography relative to poly(styrene) standards in tetrahydrofuran.

may have a slightly different hydrodynamic volume when analyzed by GPC. However, the Mark−Houwink parameters *K* and *a* are not dramatically different between poly(*t*-BuA) ($K_{\mathrm{P}t-\mathrm{BuA}} = 3.33 \times 10^{-5}$ dL g^{-1}, $a_{\mathrm{P}t-\mathrm{BuA}} = 0.80$)[65] and poly(styrene) ($K_{\mathrm{PS}} = 11.4 \times 10^{-5}$ dL g^{-1}, $a_{\mathrm{PS}} = 0.716$)[66] in THF. The PDI with added free nitroxide was initially quite high during the early stages of the polymerizations (~1.7−2.4) but smoothly decreased as the polymerization continued with PDI's in all cases reaching ~1.2. GPC chromatograms are shown in Figure 4a−f illustrating the evolution of the molecular weight distributions as a function of feed composition and additional free nitroxide. Table 3 summarizes the molecular weight distribution data for the samples given in Figure 4. Note that in each case generally the final PDI is lower with highly symmetrically peaks when using additional SG1. Also note that oligomeric products were formed even at the initial times which indicate polymerization was actually starting to occur even before the set point of 115 °C was attained. The additional free nitroxide is thus very important in this particular copolymerization in that it allows much better control of molecular weight as a function of conversion. Chain extension experiments using the copolymers as macroinitiating species made here are in progress and should provide a good test regarding the control of these systems and allow pursuit of more sophisticated architectures.

Composition of Styrene/*tert*-Butyl Acrylate Copolymers. To determine the final compositions of the copolymers, Fourier transform infrared spectroscopy (FT-IR) was useful since the distinctive carbonyl stretch at 1720 cm^{-1} can be used as a marker for the *t*-BuA concentration while the peak at 700 cm^{-1} was used as a marker for the styrene concentration in the copolymer. Figure 5 illustrates the FT-IR spectra of the polymerizations done with and without additional SG1 free nitroxide. Note that as the *t*-BuA concentration in the feed increases, the peak due to the incorporation of *t*-BuA in the copolymer becomes stronger. Table 4 indicates the compositions of the various S/*t*-BuA random copolymers synthesized for various initial feed formulations. There did not seem to be a pronounced effect on copolymer composition caused by the additional free nitroxide. At low initial *t*-BuA feed concentrations, $f_{t-\mathrm{BuA},0}$, the final molar composition of the copolymer with respect to *t*-BuA, $F_{t-\mathrm{BuA}}$, was richer than that of the feed while at higher concentrations ($f_{t-\mathrm{BuA},0} > 40\%$), the final copolymer composition became increasingly less rich in *t*-BuA compared to the feed. In order to understand more thoroughly the effect of feed composition on the microstructure for this particular comonomer pair, we performed an additional series of experiments over a wider initial feed concentration range. The relative kinetic effect on binary copolymer composition is often

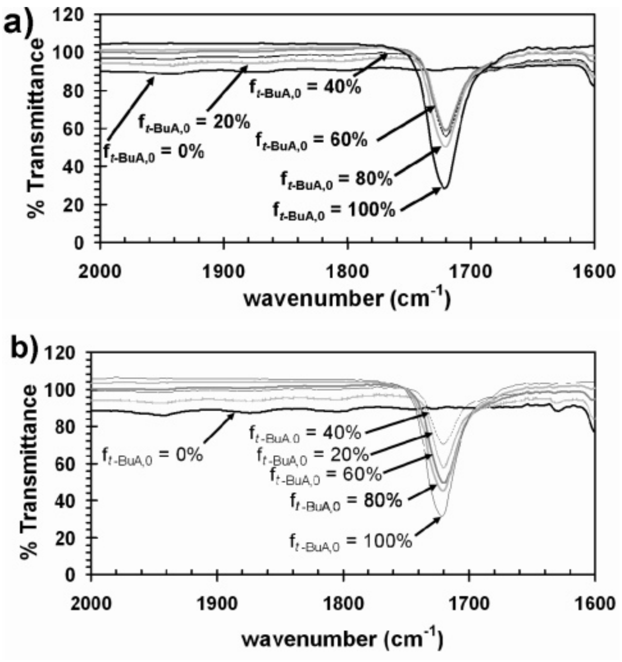

Figure 5. Fourier transform infrared spectra (FT-IR) of a series of poly(styrene-*ran*-*tert*-butyl acrylate) (P(S-*ran*-*t*-BuA) copolymers of various compositions (denoted by the initial molar feed composition of *t*-BuA, $f_{t-\mathrm{BuA},0}$) synthesized at 115 °C using (a) BlocBuilder as the sole initiator and (b) 4.5 mol % SG1 relative to BlocBuilder. Note the strong carbonyl stretch at 1720 cm^{-1} indicative of the *t*-BuA content in the final copolymer increase with increasing initial concentration of *t*-BuA in the feed.

Table 4. Composition of Styrene/*tert*-Butyl Acrylate Copolymers Synthesized in Bulk at 115 °C with BlocBuilder or SG1/ BlocBuilder Initiators

without SG1 free nitroxide		with SG1 free nitroxide ($r = 0.045$)[c]	
$f_{t-\mathrm{BuA},0}$[a]	$F_{t-\mathrm{BuA}}$[b]	$f_{t-\mathrm{BuA},0}$	$F_{t-\mathrm{BuA}}$
23	32	20	31
41	41	40	37
60	47	60	48
79	56	81	63

[a] $f_{t-\mathrm{BuA},0}$ = initial % molar fraction of *tert*-butyl acrylate in the feed. [b] $F_{t-\mathrm{BuA}}$ = molar % fraction of *tert*-butyl acrylate in the final polymer determined by Fourier transform infrared spectroscopy. [c] $r = [\mathrm{SG1}]_0/[\mathrm{BlocBuilder}]_0$.

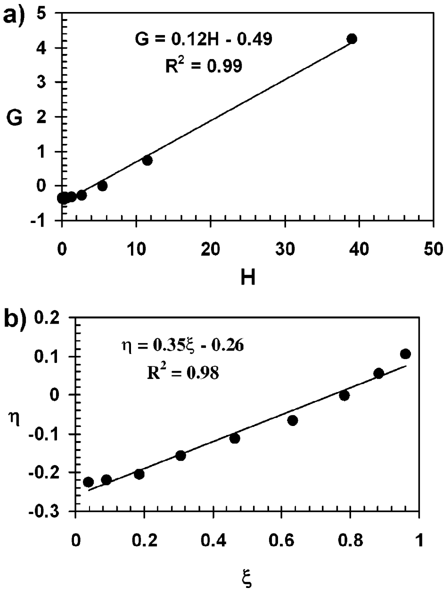

Figure 6. (a) Fineman−Ross and (b) Kelen−Tüdos plots to determine the binary reactivity ratios for *tert*-butyl acrylate and styrene for random copolymerizations done in bulk at 115 °C using BlocBuilder as the unimolecular initiator and 4.5 mol % SG1 relative to BlocBuilder (see Table 5 for properties of samples used). The theoretical molecular weight for each polymerization was ∼45 kg/mol.

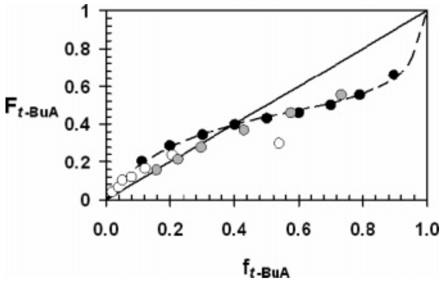

Figure 7. Mayo−Lewis plot of copolymer composition with respect to *tert*-butyl acrylate $F_{t-\mathrm{BuA}}$ vs monomer feed composition $f_{t-\mathrm{BuA}}$ ($f_{t-\mathrm{BuA}} \approx$ initial *tert*-butyl acrylate monomer feed composition $f_{t-\mathrm{BuA},0}$) using *tert*-butyl acrylate and styrene reactivity ratios determined from nonlinear least-squares fitting of the Mayo−Lewis equation to the experimental data ($r_{t-\mathrm{BuA}} = 0.10 \pm 0.01$ and $r_\mathrm{S} = 0.41 \pm 0.02$). The fit is indicated by the dashed line while the experimental data for copolymerizations done in bulk at 115 °C using BlocBuilder as the unimolecular initiator and 4.5 mol % free nitroxide SG1 relative to BlocBuilder is indicated by the solid circles. As a comparison, the data of Rätzsch and Stephan[23] for conventional radical polymerizations performed at 60 °C in toluene using benzoyl peroxide initiator indicated by the gray circles is shown along with the data of Leung et al.[68] for conventional radical polymerization performed at 70 °C in toluene using azobis(isobutyronitrile) (AIBN) initiator indicated by the open circles. The straight line indicates the azeotropic composition ($f_{t-\mathrm{BuA}} = F_{t-\mathrm{BuA}}$).

described with a simple terminal model[67] characterized by the reactivity ratios r_1 and r_2, where r_1 is the relative preference for monomer of type "1" to add onto a propagating chain with a terminal "1" group while r_2 is the relative preference for monomer of type "2" to add onto a propagating chain with a terminal "2" group. When surveying the literature to find reactivity ratios for the *t*-BuA/S binary copolymerization as a comparison, we were able to find the effect of alkyl group length of various acrylates copolymerized with styrene by conventional free radical random polymerization.[22,23] In all cases, the reactivity ratio of styrene was greater than that of any acrylate. More recently, some data for *t*-BuA/styrene conventional free radical copolymerizations in a limited feed composition range were provided but reactivity ratios were not determined.[68] For the related *n*-butyl acrylate/styrene system made by conventional free radical polymerization, $r_{n-\text{butyl acrylate}} = 0.151$ and $r_\text{styrene} = 0.747$,[25] while similar ratios were found for *n*-butyl acrylate/styrene copolymers made by atom transfer radical polymerization ($r_{n-\text{butyl acrylate}} = 0.22-0.26$, $r_\text{styrene} = 0.68-0.82$).[27] Similar ratios were obtained by conventional radical copolymerization for isobutyl acrylate/styrene ($r_{i-\text{butyl acrylate}} = 0.181$, $r_\text{styrene} = 0.720$;[25] $r_{i-\text{butyl acrylate}} = 0.17$, $r_\text{styrene} = 0.73$[23]). The *tert*-butyl acrylate/styrene system copolymerized in toluene at 60 °C by conventional radical polymerization was reported to have a slightly higher reactivity ratio for *tert*-butyl acrylate compared to the other acrylates with styrene ($r_{t-\mathrm{BuA}} = 0.29$, $r_\mathrm{S} = 0.89$).[23]

To determine the reactivity ratios for the *tert*-butyl acrylate/styrene system, we used the Mayo−Lewis[67] equation to relate the instantaneous monomer feed compositions f_1 and f_2 to the copolymer composition F where the subscript "1" refers to monomer of type 1 and "2" refers to monomer of type 2. Note that f_1 and f_2 were approximated by the initial monomer feed composition since conversion was kept low.

$$F_1 = \frac{r_1 f_1^{\,2} + f_1 f_2}{r_1 f_1^{\,2} + 2 f_1 f_2 + r_2 f_2^{\,2}} \tag{3}$$

A number of different approaches have been applied to determine the reactivity ratios. The Fineman−Ross approach[69] linearizes the Mayo−Lewis equation which after the appropriate plot of the variables G and H defined in eq 4 will provide a linear relationship giving the reactivity ratios as the slope and intercept.

$$G = \frac{f_1}{f_2}\frac{2F_1 - 1}{F_1}, \quad H = \left(\frac{f_1}{f_2}\right)^2 \frac{1 - F_1}{F_1} \tag{4}$$

$$G = r_1 H - r_2 \tag{5}$$

However, the Fineman−Ross approach is generally biased toward samples at low f_1 being weighted more heavily with a consequently poor fit of the data. Later, Kelen and Tüdos[70] reduced the bias introduced by the Fineman−Ross method by introducing an arbitrary constant α which provides equal weighting to all observations. The variables for the Kelen−Tüdos plot are shown in eq 6.

$$\eta = \left[r_1 + \frac{r_2}{\alpha}\right]\epsilon - \frac{r_2}{\alpha} \tag{6}$$

In this case, the reactivity ratios r_1 and r_2 refer to those of *tert*-butyl acrylate and styrene, respectively. The parameters η, ϵ,

Table 5. Composition of *tert*-Butyl Acrylate/Styrene Random Copolymers Synthesized at 115 °C in Bulk with BlocBuilder and Additional SG1 Free Nitroxide

$f_{t-\mathrm{BuA},0}$[a]	$F_{t-\mathrm{BuA}}$[b]	conversion (X)	M_n (g/mol)[c]	M_w (g/mol)[c]	PDI[c]
0	0	0.13	6500	8400	1.31
11.1	20.5 ± 0.4	0.17 ± 0.03	6800 ± 1800	8700 ± 1600	1.31 ± 0.14
19.9	28.7 ± 0.5	0.14 ± 0.03	6200 ± 1700	8200 ± 1500	1.35 ± 0.11
30.1	34.5 ± 0.3	0.12 ± 0.03	7000 ± 1600	8900 ± 1600	1.29 ± 0.08
40.1	39.6 ± 0.6	0.14 ± 0.01	5800 ± 1000	8000 ± 800	1.39 ± 0.10
50.1	43.1 ± 0.4	0.12 ± 0.03	7700 ± 1100	10000 ± 1200	1.30 ± 0.04
60.0	45.8 ± 0.3	0.15 ± 0.04	7600 ± 1700	9900 ± 1700	1.32 ± 0.09
70.1	49.8 ± 0.9	0.16 ± 0.03	7400 ± 1300	9900 ± 1300	1.34 ± 0.08
79.1	55.2 ± 0.6	0.14 ± 0.02	6600 ± 1500	9300 ± 1400	1.43 ± 0.14
89.7	66.0 ± 0.2	0.12 ± 0.03	7900 ± 1500	10800 ± 1700	1.37 ± 0.06
100	100	0.16	11300	15100	1.34

[a] $f_{t-\mathrm{BuA},0}$ = initial % molar fraction of *tert*-butyl acrylate in the feed. [b] $F_{t-\mathrm{BuA}}$ = molar % fraction of *tert*-butyl acrylate in the final polymer determined by Fourier transform infrared spectroscopy. [c] Number-average (M_n), weight-average (M_w) molecular weight, and polydispersity index (M_w/M_n) determined by gel permeation chromatography relative to poly(styrene) standards in tetrahydrofuran.

and the scaling parameter α are proportional to the parameters G and H defined above.

$$\eta = \frac{G}{\alpha + H}, \quad \epsilon = \frac{H}{\alpha + H} \tag{7}$$

$$\alpha = \sqrt{H_{\min} H_{\max}} \tag{8}$$

Note that $H_{\min}$ and $H_{\max}$ refer to the minimum and maximum H values determined from the data. Fineman−Ross and Kelen−Tüdos plots are shown in Figure 6 and yield $r_{t-\mathrm{BuA}} = 0.12 \pm 0.004$ and $r_S = 0.49 \pm 0.05$ for the Fineman−Ross method and $r_{t-\mathrm{BuA}} = 0.09 \pm 0.02$ and $r_S = 0.40 \pm 0.02$ for the Kelen−Tüdos method. Despite its improvement over the Fineman−Ross method, the Kelen−Tüdos method is still a linearization, and a nonlinear least-squares fit to the Mayo−Lewis equation is likely the most statistically sound method to obtain the desired parameters.[71] Thus, we proceeded to use the reactivity ratios estimated from the Kelen−Tüdos plot as initial guesses for the nonlinear least-squares fitting of the data using a commercial software package (SigmaPlot 10.0). The minimum error converged after six iterations yielding reactivity ratios $r_{t-\mathrm{BuA}} = 0.10 \pm 0.01$ and $r_S = 0.41 \pm 0.02$, which are not too dissimilar from those obtained by the other methods. The Mayo−Lewis plot is shown in Figure 7 using the reactivity ratios from the nonlinear least-squares fit with our experimental data and compared with the results of Rätzsch and Stephan[23] and Leung et al.[68] Several possible reasons exist for the difference in reactivity ratios between those reported here and from those reported by Rätzsch and Stephan.[23] The earlier study examined copolymerizations done at 60 °C in toluene using conventional radical polymerization while the present study examined copolymerizations done at 115 °C in bulk using controlled radical polymerization. The differences in temperature and solvent may alter the absolute values of the reactivity ratios somewhat although in both cases $r_{t-\mathrm{BuA}} < r_S$ and $r_{t-\mathrm{BuA}}, r_S < 1$.

Conclusions

The addition of 4.5 mol % SG1 free nitroxide with regards to the BlocBuilder initiator moderated the rate of the bulk polymerization of *tert*-butyl acrylate (*t*-BuA) and *t*-BuA/styrene copolymers. With the additional free nitroxide, the polymerization at 115 °C was slower and more controlled with polydispersity indices typically ∼1.2. The result of adding free nitroxide demonstrated a controlled radical polymerization process with the number-average molecular weight $\bar{M}_n$ increasing linearly with overall monomer conversion up to ∼50%, which was clearly not the case when the free SG1 nitroxide was omitted. In all cases with or without the addition of free SG1 nitroxide, the feed composition had little effect on the experimentally obtained $\bar{M}_n$ and conversion data although there was a wider dispersion in the data for experiments without free nitroxide. The apparent rate constants were slightly greater without the additional SG1 free nitroxide. The kinetics of the nitroxide-mediated polymerization of *t*-BuA were different than that of other acrylates in that the propagation rate constant k_p was between that of styrene and other acrylates such as *n*-butyl acrylate (*n*-BuA) and acrylic acid. The product of k_p with the equilibrium constant K was $k_pK = (3.0 \pm 0.3) \times 10^{-6}\ \mathrm{s}^{-1}$ for *t*-BuA at 115 °C in bulk and was similar to that of styrene but much lower compared to *n*-BuA or acrylic acid, which suggests *t*-BuA polymerization is characterized by a moderate k_p and low K. This feature may be advantageous for avoiding excessive exotherms as is the case for acrylic acid polymerizations, for example. Copolymer compositions determined using Fourier transform infrared spectroscopy (FT-IR) indicated that *t*-BuA/styrene random copolymer reactivity ratios $r_{t-\mathrm{BuA}}$ and r_S were <1 with $r_{t-\mathrm{BuA}} < r_S$. The final copolymer compositions were not significantly affected by the use of the additional SG1 free nitroxide. The *t*-BuA/styrene reactivity ratios determined for BlocBuilder-initiated controlled free radical polymerization at 115 °C in bulk using the various methods such as Fineman−Ross, Kelen−Tüdos, and nonlinear least-squares minimization were in the ranges $r_{t-\mathrm{BuA}} = 0.09−0.12$ and $r_S = 0.40−0.49$.

Acknowledgment. This work was supported by the Canada Foundation for Innovation (CFI) New Opportunities Fund and NSERC Discovery Grant. B.L. and A.G. acknowledge scholarship support from the Department of Chemical Engineering, McGill University, and the authors thank Petr Fiurasek for his assistance with the FTIR measurements and Scott Schmidt and Noah Macy of Arkema, Inc., for their aid in obtaining the BlocBuilder and SG1 mediators for this work.

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MA071689W