Styrene/Acrylic Acid Random Copolymers Synthesized by Nitroxide Mediated Polymerization: Effect of Free Nitroxide on Kinetics and Copolymer Composition

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ABSTRACT: Styrene/acrylic acid (S/AA) mixtures were copolymerized in concentrated 50 wt% 1,4-dioxane solutions at 120ºC at two ratios of additional free nitroxide mediator, N,N-*tert*-butyl-N-[1'-diethylphosphono-2,2'-dimethylpropyl]nitroxide (SG1), relative to 2-[N-*tert*-butyl-2,2-(dimethylpropyl)aminooxy] propionic acid (BlocBuilder®, Arkema) alkoxyamine unimolecular initiator (4.5 and 9 mol% [SG1]/[BlocBuilder®]). Without SG1 at initial acrylic acid monomer feed concentrations $f_{AA,0} > 40$ mol%, the apparent rate constants increased sharply, noticeable exotherms were observed and polydispersities increased from 1.20 at $f_{AA,0} = 0$ mol% to 1.48 at $f_{AA,0} = 80$ mol%. With 4.5 mol% [SG1]/ [BlocBuilder®], polymerization rates were slower and not as strongly affected by $f_{AA,0}$ although exotherms were still noticeable at high $f_{AA,0}$. Polydispersities remained ~ 1.3 and only increased to > 1.4 at high conversions for $f_{AA,0} = 80$ mol%. Exotherms were rendered nearly negligible when 9 mol% [SG1]/[BlocBuilder®] was used, leading to copolymers with much narrower molecular weight distributions and k_pK values for co-monomer mixtures bracketed between those of styrene and acrylic acid homopolymerizations at 120^{o}C (k_p = propagation rate constant, K = equilibrium constant). Copolymer reactivity ratios estimated for samples produced using 9 mol% [SG1]/[BlocBuilder®] by non-linear least squares minimization were $r_{AA} = 0.25\pm0.11$, $r_S = 0.93\pm0.0.37$, in agreement with previous literature.

INTRODUCTION

Functional group segments such as acids and bases find wide ranging application in structures templated from block copolymer morphologies such as next-generation separations media[1,2], controlled release[3-5], catalyst supports[6] and nano-reactors[7]. Simultaneously, enormous advances in controlled free radical polymerization chemistry has made synthesis of such functional block copolymers much easier[8-11]. With controlled free radical polymerization, the manipulation of molecular weight distribution and microstructure typically required for effective block copolymer self-assembly approaches that achieved by ionic polymerization without rigorous reagent purification, protection of functional groups and scrupulously clean transfers associated with ionic polymerization processes[12]. Further, some combination of monomers (such as acrylic acid and styrene) and sequences that cannot be polymerized by ionic polymerization can be polymerized directly by controlled radical polymerizations. We are interested in incorporating acrylic acid functional groups into segmented or tapered block copolymers to be ultimately used for some of the applications cited. Acrylic acid has been polymerized and/or copolymerized with other monomers by controlled radical polymerization processes such as nitroxide mediated polymerization (NMP)[13-17], reversible addition fragmentation transfer (RAFT)[18-21] and to some degree, atom transfer radical polymerization (ATRP)[22]. The latter method is rather difficult to apply due to poisoning of the metal/ligand catalyst by the acrylic acid.

Traditionally, NMP is limited to styrenic-based monomers[8,9,23-28] using 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) free radical as the mediator at temperatures > 125°C. NMP routes to incorporate other commercially important monomers such as acrylates were intensely focused on developing mediators that improve the rate of mediator homolysis and allow controlled polymerization of such monomers. Consequently, acyclic β-phosphonylated nitroxides such as N-*tert*-butyl-N-[1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide (also known as SG1) (Figure 1a) were developed that could polymerize acrylates such as n-butyl acrylate using temperatures as low as 90°C[29-32]. Currently, some SG1-based unimolecular initiators are available to directly polymerize acrylic acid. Couvreur et al used the SG1-based alkoxyamine, N-*tert*-butyl-N-1-diethylphosphono-2,2-

dimethylpropyl-O-1-methoxycarbonylethylhydroxylamine, known as MONAMS (Figure 1b) with a small excess of free SG1 nitroxide (9 mol% SG1 relative to MONAMS) to polymerize acrylic acid at a monomer loading of 21 wt% at 120°C with molecular weights up to about 10^4 g/mol and polydispersities in the range from 1.3-1.4[13]. A small excess of free nitroxide was deemed necessary to control the polymerization rate and retain characteristics of pseudo-“living” behavior (linear increase in molecular weight with conversion and narrow molecular weight distribution). Couvreur et al copolymerized a broad range of styrene/acrylic acid feed compositions (10/90 to 90/10 acrylic acid/styrene) using SG1/MONAMS (4.5 mol% SG1 relative to MONAMS) at 120°C at a monomer loading of approximately 25 wt% in 1,4-dioxane with target molecular weights up to 1.1 x 10^4 g/mol[14]. Polymerization kinetics did not vary greatly with feed composition and polydispersities ranged from 1.2 to 1.4 Since then, more potent mediators have been developed such as the isobutyric acid adduct with SG1, 2-[N-*tert*-butyl-2,2-dimethylpropyl)aminoxy] propionic acid known as BlocBuilder®[32-35] (Figure 1c). Styrene and/or n-butyl acrylate polymerizations have been the focus of its application thus far, particularly in mini-emulsion systems due to its water solubility when neutralized[15,34,35]. Nicolas et al. made BlocBuilder® soluble in water by neutralization with sodium hydroxide solution and the resulting initiator was able to regulate the polymerization of n-butyl acrylate and styrene without additional free nitroxide as was required for polymerizations with MONAMS[15]. Lefay et al. showed that a poly(acrylic acid) synthesized with MONAMS and 9 mol% SG1 free nitroxide relative to MONAMS has sufficiently active alkoxyamine end-groups to be used as a macro-initiator for styrene and n-butyl acrylate polymerization[16]. Later, the same group used BlocBuilder® and 5 mol% SG1 to initiate the nitroxide-mediated polymerization of a styrene-acrylic acid random copolymer with number average molecular weight 6.5 x 10^3 g/mol and polydispersity index = 1.5 which was an efficient stabilizer for emulsion polymerizations of styrene/methylmethacrylate and styrene/n-butyl acrylate mixtures using as little as 3-4 wt% relative to monomer as an emulsifier[17].

It is thus of interest to observe how effective BlocBuilder® is at controlling the polymerization of monomers such as acrylic acid and *tert*-butyl acrylate, which we reported in a related publication[36].

Compared to *tert*-butyl acrylate, direct polymerization of acrylic acid is attractive to avoid the subsequent cleavage of the *tert*-butyl group to produce the desired acidic group. In order to test the effectiveness of BlocBuilder® and BlocBuilder®/SG1 compared to the MONAMS/SG1 mixed unimolecular initiator/mediator for styrene/acrylic acid compositions[14], we initially examined a much higher concentration of monomer in the feed (about 50 wt% compared to 21 wt% for previous studies) in addition to using no additional free nitroxide to control the polymerization. The following study of the copolymerization kinetics and associated effect on copolymer composition will greatly assist in the design of sequenced or tapered block copolymers where placement of the acrylic acid concentration along the chain is vital for the performance of the material.

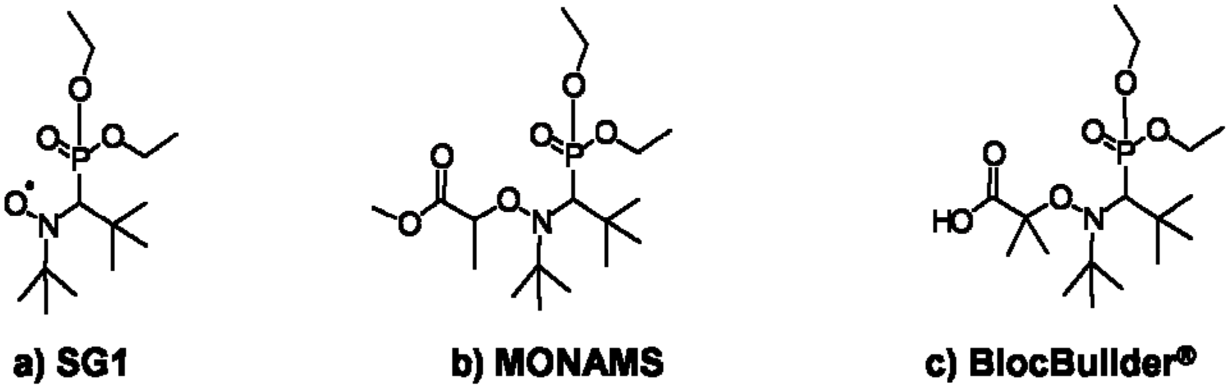

Figure 1: Structures of various alkoxyamine mediators and unimolecular initiators used for nitroxide-mediated controlled radical polymerization: a) N-*tert*-Butyl-N-[1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide (SG1); b) N-*tert*-Butyl-N-1-diethylphosphono-2,2-dimethylpropyl-O-1-methoxycarbonylethylhydroxylamine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

EXPERIMENTAL SECTION

Materials. 1,4-Dioxane (99.7%), calcium hydride (90-95% reagent grade), basic alumina (Brockmann, Type 1, 150 mesh), trimethylsilyldiazomethane (2 M solution in hexane) were received from Aldrich and used as received. Hexane (98.5%) and methanol (99.8%) were obtained from Fisher and used as received. Acrylic acid (99%) was obtained from Fluka and used as received. 2-[N-*tert*-Butyl-2,2-

dimethylpropyl)aminoxy] propionic acid, (99%, BlocBuilder®) was obtained from Arkema and N-*tert*-butyl-N-[1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide (85%, SG1) was kindly donated by Noah Macy from Arkema and used as received. Styrene (99%, Aldrich) was purified by passage through a column of 5% calcium hydride/basic alumina and stored in a sealed flask in a refrigerator under a head of nitrogen until required.

Synthesis of Acrylic Acid/Styrene Random Copolymers. The total concentration of monomer in the solution was 50 wt% in each case. The amounts of BlocBuilder®, acrylic acid (AA) and styrene were calculated so that the target molecular weight was about 45 kg/mol in each case. Detailed experimental conditions regarding the feed compositions are listed in Table 1. Note the concentrations of BlocBuilder® and SG1 were kept constant. A formulation with an acrylic acid initial feed concentration ($f_{AA,0}$) of 60 mol% and 4.5 mol% SG1 additional free nitroxide relative to BlocBuilder® is given as an example below.

To a 100 mL two neck glass round bottom flask equipped with a condenser, magnetic stir bar and thermal well, was added BlocBuilder® (0.230 g, 0.604 mmol), SG1 (0.008 g, 0.027 mmol), acrylic acid (AA) (13.83 g, 192 mmol) and 1,4 dioxane (27.10 g, 308 mmol) and then sealed with a rubber septum. The reactor was placed inside a heating mantle and a thermocouple was placed inside the temperature well and then connected to a temperature controller. A 90/10 w/w glycol/water mixture using a Neslab 740 refrigerating unit was then circulated through the condenser to prevent any evaporation during the reaction. Previously purified styrene (13.4 g, 129 mmol) was transferred to the reactor in the desired amount by cannula and mixing of the monomers, mediator and solvent commenced. A purge of ultra pure nitrogen was then applied to the reactor for 30 minutes at room temperature. Heating of the reactor contents at a rate of about 8°C/min was then started to 120°C while maintaining the nitrogen purge. The time at which the reactor temperature reached 110°C was taken as the start of the reaction since we found some polymer already being formed at the initial time when 120°C was attained. Samples were periodically removed by syringe and the polymer was precipitated in hexane. After filtration and recovery, the precipitated polymer was dried in a vacuum oven at 60°C until constant weight was attained to remove any solvent and unreacted monomer. The final yield for the example given was 74% (19.0 g) after 75 minutes of polymerization with number average molecular weight $\overline{M}_n$ = 24.3 kg/mol, weight average molecular weight $\overline{M}_w$ = 32.6 kg/mol and polydispersity index ($\overline{M}_w / \overline{M}_n$) = 1.34 as determined by gel permeation chromatography (GPC) relative to poly(styrene) standards. The composition of the copolymer as determined by ^{1}H NMR in deuterated acetone was 44 mol% acrylic acid.

Characterization. Conversion was determined gravimetrically. To obtain the molecular weight distribution, gel permeation chromatography (GPC) using tetrahydrofuran (THF) as the mobile phase was employed. However, the poly(styrene-*ran*-acrylic acid) (P(S-r-AA)) samples, particularly at high AA feed concentrations, needed to be derivatized in order to be soluble in organic solvents such as THF. The procedure used by Couvreur et al. was employed in which the acrylic acid groups were methylated after treatment with trimethylsilyldiazomethane (TMS-diazomethane)[14]. The various copolymers were dissolved in mixtures of THF with varying amounts of distilled water in order to solubilize the block copolymer. The solution of TMS-diazomethane was then added dropwise to the samples. Bubbling was observed due to the gas evolved when TMS-diazomethane reacts with the acidic groups in the copolymer. Additional TMS-diazomethane was added until the bubbling stopped. Excess TMS-diazomethane was then added and the solution was allowed to sit for several hours. The derivatized polymer was then precipitated in hexane, recovered and dried under vacuum at 60^{o}C for 24 h. The dry, derivatized polymer was then dissolved in THF for molecular weight analysis with GPC. A Waters Breeze system was used at a mobile phase flow rate of 0.3 mL/min equipped with 3 Styragel® HR columns (HR1 with molecular weight measurement range of 10^2 – 5 x 10^3 g/mol, HR2 with molecular weight measurement range of 5 x 10^2 – 2 x 10^4 g/mol and HR4 with molecular weight measurement range 5 x 10^3 – 6 x 10^5 g/mol) and a guard column. The molecular weight was determined using calibration relative to narrow molecular weight distribution poly(styrene) standards. The GPC was equipped with a Waters 2487 UV detector set at a wavelength of 255 nm to detect aromatic groups and RI 2410 differential refractive index (RI) detectors. ^{1}H NMR spectroscopy was performed using a 200MHz Varian Gemini 2000 spectrometer. Typically, 10 mg of the copolymer sample was dissolved in 0.7 ml deuterated acetone (d_6-acetone, Cambridge Isotope Laboratories) in 5mm 508 Up NMR tubes. The samples were injected into the probe, shimmed and scanned 32 times. ^{1}H NMR in $CDCl_3$ was also performed after methylation of the acrylic acid units in the random copolymers which has been shown to be quantitative in previous studies[14]. Composition determination by ^{1}H NMR of the methylated copolymers in $CDCl_3$ agreed well with the compositions determined using ^{1}H NMR of the acrylic acid/styrene copolymers in deuterated acetone.

Styrene/Acrylic Acid Copolymer Composition Determination. To determine the copolymer reactivity ratios, polymerizations were conducted in the same 100 mL round-bottom flask and experimental set-up used for the kinetic experiments. All polymerizations were done at low conversions in order to avoid compositional drift corrections necessary for calculation of reactivity ratios. Consequently, all copolymerizations for reactivity ratio determination were done for no more than 15 minutes at 120°C in 50 wt% 1,4 dioxane solution with BlocBuilder® and 9 mol% additional SG1 free nitroxide only. The high ratio of SG1/BlocBuilder® ensured that nearly isothermal conditions were achieved. Six initial feed compositions (initial acrylic acid molar monomer feed compositions of 12.2%, 19.9%, 41.1%, 60.3%, 80.0% and 90.5%) were studied to compare copolymer composition to previous styrene/acrylic acid copolymerizations done in more dilute solutions with a different unimolecular initiator[14]. The target molecular weight was identical to that used in the kinetic experiments described earlier (45 kg/mol). A sample synthesis using an acrylic acid initial molar feed fraction of 40% is given as an example. To the reactor was added 0.144 g (0.38 mmol) BlocBuilder®, 0.010 g (0.034 mmol) of SG1 free nitroxide, 5.64 g (0.078 mol) acrylic acid, 11.66 g (0.11 mol) of previously purified styrene and 17.0 g of 1,4-dioxane solvent. The reactor was sealed with a rubber septum, connected to a condenser and a re-circulating chiller (Neslab 740) and purged with nitrogen for 30 minutes. Heating was then started using a temperature controller with a set-point set of 120°C while allowing the nitrogen purge to continue. Heating occurred at a rate of about 10°C/min. The initial time of polymerization was taken when the reactor temperature reached 110°C. After 15 minutes, samples were taken by syringe from the reactor (~ 0.3 mL) and were then precipitated in previously weighed 4 mL vials containing excess hexane to allow for gravimetric determination of yield. The samples were placed in a vacuum oven overnight at 70°C to remove solvent and residual monomer. The yield for the particular sample was 0.021 g by gravimetry corresponding to a conversion of 9.6%. Molecular weight measurements were done using gel permeation chromatography (GPC) relative to poly(styrene) standards in THF at 40°C after treatment with TMS-diazomethane as described earlier in the experimental section. For the particular sample, GPC measurements revealed the particular copolymer had number average molecular weight M_n = 4.9 kg/mol, weight average molecular weight M_w = 6.1 kg/mol and polydispersity index (PDI = M_w/M_n) of 1.25. Once dried, the samples were examined by ^{1}H NMR using d_6-acetone as the solvent and the copolymer composition determined by taking the ratio of the methine proton from the poly(acrylic acid) (δ = 2.4 ppm, m, C***H***-COOH) to that of the aromatic protons from poly(styrene) (δ = 6.8-7.1 ppm, b, aromatic). Chemical shifts were observed in all the spectra corresponding to residual 1,4-dioxane solvent (δ = 3.8 ppm) and d_6-acetone (δ = 2.0 ppm). For the specific example given for an initial molar feed fraction of 41.1 mol% acrylic acid, the final copolymer composition was 42.3 mol% as determined by ^{1}H NMR.

RESULTS AND DISCUSSION

Kinetics of Styrene/Acrylic Acid Copolymerization. Table 1 indicates the formulations for the various styrene/acrylic acid random copolymers used in the kinetic experiments. Note that the target molecular weight was kept constant and the monomer feed concentration studied was 50 wt%. Consequently, total monomer molar concentrations varied somewhat but were in the range between 5-6 mol·L^{-1} for 50 wt% monomer feed in solution. Semi-logarithmic kinetic plots of monomer conversion versus time for the various experiments are indicated in Figure 2 while Figure 3 compares the product of the propagation rate constant k_p with the equilibrium constant K between dormant and active chains, k_pK as a function of feed composition and added free nitroxide. The apparent rate constants $k_p[P^\bullet]$ (where k_p is the propagation rate constant and $[P^\bullet]$ is the concentration of growing chains) were used to derive the k_pK values (see Table 2). Molecular weight and polydispersity index versus conversion are plotted in Figures 4 and 5 as a function of feed composition, respectively. GPC chromatograms shown in Figure 6 along with tabulated molecular weight data in Table 3 compare the effect of adding SG1 free nitroxide on samples taking at various polymerization times for the highest acrylic acid monomer feed fraction studied of 80 mol%.

Effect of Additional Free Nitroxide on Kinetics. The effect of the feed composition on the reaction kinetics was more pronounced without the use of any free nitroxide (Figure 2a) compared to the addition of 4.5 mol% free SG1 nitroxide relative to BlocBuilder® (Figure 2b) or 9.0 mol% free SG1 nitroxide relative to BlocBuilder® (Figure 2c). Higher conversion rates were obtained at shorter polymerization times without the use of additional free nitroxide. Estimation of kinetic parameters was done by plotting ln(1/(1-x)) versus time in the linear region which yielded a slope equal to $k_p[P^\bullet]$ where x is the conversion, k_p is the propagation rate constant and $[P^\bullet]$ is the concentration of propagating macro-radicals. The effect of the additional free nitroxide was to shift the equilibrium between dormant and active chains so that the propagating macro-radical is in the dormant state more often, thus effectively reducing the propagation rate and allowing a slower, more controlled polymerization.

Comparison of the apparent rate constants $k_p[P^\bullet]$ summarized in Table 2 indicates that the slopes are higher without the additional free nitroxide, particular at higher acrylic acid feed concentrations. We noticed higher exotherms at higher initial acrylic acid feed compositions, particularly without any additional free nitroxide but less so with 4.5 mol% free SG1 nitroxide. Exotherms approaching > 15-20°C were observed which is quite significant considering the small size of the reactor we used where heat transfer was expected to be quite efficient. However, when the polymerization was performed with 9 mol% free SG1 nitroxide, the polymerization rates were relatively insensitive to acrylic acid feed composition and the exotherms were negligible, being only 2-3°C for a short period of time at the highest acrylic acid feed composition of 80 mol% studied.

Acrylic acid, like other acrylates such as n-butyl acrylate ($k_p = 1 \times 10^5$ $L \cdot mol^{-1} \cdot s^{-1}$ at 120°C)[37] has a relatively high k_p ($2\text{-}3 \times 10^5$ $L \cdot mol^{-1} \cdot s^{-1}$ at 120°C)[38] compared to styrene (2×10^3 $L \cdot mol^{-1} \cdot s^{-1}$ at

120°C)[39]. For monomers with high k_p values in the absence of free nitroxide, the propagating radicals increase in concentration and then decrease due to irreversible self-termination reactions while the nitroxide concentration builds up (i.e. the persistent radical effect[26,40-42]). During this period, there may not be sufficient nitroxide to trap the remaining propagating radicals if the k_p of the monomer is too high. Consequently, highly exothermic conditions would result and this was noticed in our experiments without any free nitroxide or with 4.5 mol% SG1/BlocBuilder® at high initial acrylic acid feed concentrations such as 80 mol% of acrylic acid. Since the temperature increases for this situation, the k_p increases and this caused the sharp increase in $k_p[P^\bullet]$ observed at high acrylic acid feed concentrations without any additional free nitroxide. With the addition of 9.0 mol% SG1 free nitroxide, $k_p[P^\bullet]$ is much less sensitive to the initial molar feed fraction of acrylic acid and is in agreement with previous studies using lower monomer concentrations[14] which showed little change in $k_p[P^\bullet]$ as a function of initial acrylic acid feed composition. This lack of sensitivity was attributed to the significantly lower equilibrium constant K between dormant and active chains for acrylic acid compared to styrene[14]. The use of free nitroxide was thus important in regulating the polymerization rate and avoiding potentially dangerous exotherms for this particular copolymerization.

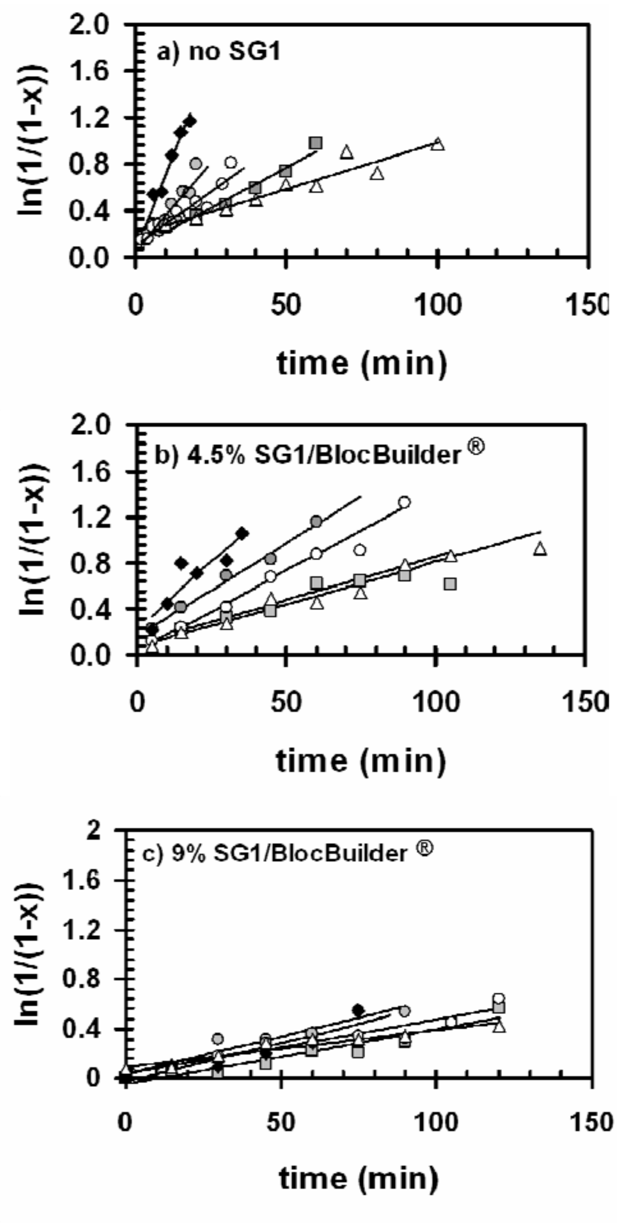

Figure 2: Scaled conversion ($\ln(1-x)^{-1}$) (x = monomer conversion) versus time for styrene-acrylic acid (S-r-AA) random copolymerizations of various feed compositions done in 50 wt% 1,4-dioxane solution at 120°C a) without any free SG1 nitroxide, b) with 4.5 mol% SG1 relative to BlocBuilder® and c) with 9.0 mol% SG1 relative to BlocBuilder®. The solid lines are linear fits to the data taken at early times used to calculate apparent rate constants $k_p[P^{\bullet}]$ where k_p is the propagation rate constant and $[P^{\bullet}]$ is the concentration of propagating macro-radicals. The initial monomer feed molar fraction of acrylic acid $f_{AA,0}$ indicated for each set in the figure correspond to $f_{AA,0}$ = 0 mol% (△), $f_{AA,0}$ = 20 mol% (□), $f_{AA,0}$ = 40 mol% (○), $f_{AA,0}$ = 60 mol% (●) and $f_{AA,0}$ = 80 mol%(♦).

At low initial acrylic acid feed concentrations for systems mediated by BlocBuilder® and SG1/ BlocBuilder®, agreement was good between the values of $k_p[P^\bullet]$ determined here with those reported elsewhere using SG1/MONAMS[14-15]. The styrene homopolymerization with BlocBuilder® has a $k_p[P^\bullet] = 1.3 \times 10^{-4}\ s^{-1}$ and with SG1/BlocBuilder® (r = 0.045) has a $k_p[P^\bullet] = 1.1 \times 10^{-4}\ s^{-1}$, both of which are in agreement with that reported by Nicolas et al who reported $k_p[P^\bullet] = 9.8 \times 10^{-5}\ s^{-1}$ using the identical BlocBuilder® initiator in bulk at 120°C[15]. At the highest ratio of SG1/BlocBuilder® studied (r = 0.09) $k_p[P^\bullet] = 5.0 \times 10^{-5}\ s^{-1}$ which is reasonable compared to the data at the lower SG1/BlocBuilder® ratio. A better comparison to account for the different SG1/BlocBuilder® ratio is to estimate the product k_pK where K is the equilibrium constant defined by Equation [1] given the equilibrium between the dormant and active species[13]:

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

where [SG1] is the concentration of free nitroxide and [P-SG1] is the concentration of the polymer-SG1 capped species. Multiplying Equation [1] by k_p gives Equation [2]:

$$k_p K = \frac{k_p[P^\bullet][SG1]}{[P - SG1]} \qquad [2].$$

Assuming that [SG1] should remain relatively close to that initially ($[SG1]_0$) and also taking [P-SG1] to be nearly the same initial concentration as the BlocBuilder® unimolecular initiator if the polymerization is assumed to be pseudo-“living” ([P-SG1] = $[\text{BlocBuilder}^®]_0$), Equation [2] is converted to the following form which allows determination of k_pK.

$$k_p K \cong k_p \frac{[P^\bullet][SG1]_0}{[BlocBuilder]_0} = k_p[P^\bullet]r \qquad [3]$$

The assumption regarding $[SG1] \approx [SG1]_0$ may be quite crude for this particular polymerization since the acrylic acid is known to react with the SG1 free nitroxide[43], thereby lowering its actual concentration in solution and resulting in an acrylic acid concentration dependent r value. Consequently, k_pK values may be overestimated for compositions with high acrylic acid feeds. Electron spin resonance (ESR) measurements would confirm if the pseudo-“living” assumption could be justified. Here, we tested the validity of this pseudo-“living” assumption in a given conversion range if the number average molecular weight M_n increased linearly with conversion as shown in Figure 4.

Here, r = $[SG1]_0/[BlocBuilder^{®}]_0$ = 0.045 and 0.09 for the experiments performed. Given k_pK for styrene[15] ($k_pK = 4.8 \times 10^{-6}$ s^{-1}) and for acrylic acid[13] ($k_pK = 1.5 \times 10^{-5}$ s^{-1}) homopolymerizations at 120°C, our data reveals that the k_pK values determined for styrene here (see Table 2) agree well with the literature value while k_pK determined at 80 mol% initial acrylic acid feed concentration was slightly higher ($k_pK = 1.7 \times 10^{-5}$ s^{-1}) than that determined for pure acrylic acid at the same temperature ($k_pK = 1.5 \times 10^{-5}$ s^{-1})[13] for r = 0.045. This discrepancy is likely due to the high monomer loading which caused the observed exotherms and increased the k_p. Further, our calculated k_pK values may be overestimated due to the loss of free nitroxide by reaction with the organic acid as mentioned previously[43]. The assumption of the constant r value at high acrylic acid feed concentrations together with the observed exotherms may misleadingly suggest that the k_pK values are functions of the concentration of SG1 in acrylic acid rich feed mixtures. With a higher concentration of SG1 free nitroxide (r = 0.09), the exotherms were less noticeable in the concentrated solutions examined and the relative decrease in active SG1 free nitroxide due to degradative reaction with acrylic acid was not as dramatic. The k_pK values consequently for the various initial feed concentrations were bracketed well by that of pure styrene and pure acrylic acid as indicated in Figure 3.

The pseudo-“livingness” of the polymerizations was tested by plotting the number average molecular weight M_n obtained from GPC measurements against the conversion (Figure 4). At low conversions in the absence of free nitroxide, the relationship was linear but started to deviate once the conversion increased to above 40% (Figure 4a-b). The controlled nature of the polymerization tended to improve with more added SG1 as indicated in Figure 4c) where little deviation was observed in the conversion range of the samples. The M_n values for copolymerizations done with r = 0.09 seem higher than those done with r = 0.045 or no SG1 for a given conversion. This observation may be attributed to the prevalence of termination reactions when less SG1 was used to control the polymerization, resulting in more dead chains as the polymerization progressed which is evident in the deviation from linearity of M_n versus conversion plots with no SG1 or with r = 0.045.

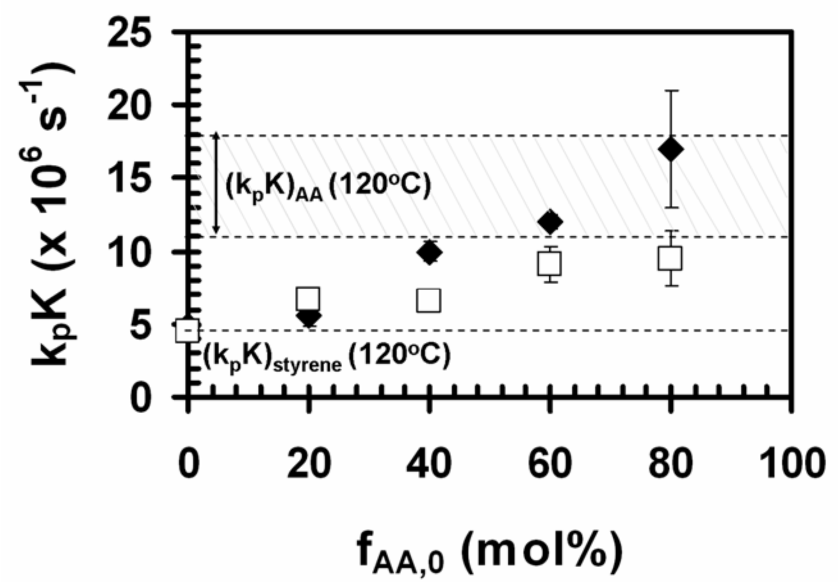

Figure 3: Product of propagation rate constant k_p and equilibrium constant K (k_pK) versus % acrylic acid molar feed fraction $f_{AA,0}$ for styrene/acrylic acid compositions copolymerized at 120°C in 50 wt% 1,4-dioxane solution as a function of added SG1 free nitroxide (4.5 mol% SG1 relative to BlocBuilder® indicated by filled diamonds (♦) and 9.0 mol% SG1 relative to BlocBuilder® indicated by open squares (□)). The dashed lines indicate the k_pK value for pure styrene ($k_pK_{styrene}$) at 120°C[15] and the range of k_pK values for acrylic acid (k_pK_{AA}) in the hatched area corresponds to the literature values found for pure acrylic acid feeds at 120°C[13].

Additional confirmation of the improvement in control could be seen by the breadth of the molecular weight distributions as indicated by the polydispersity index (PDI) which is the ratio of the weight average molecular weight M_w relative to the number average molecular weight M_n. The PDI versus conversion at various feed compositions without any free nitroxide shown in Figure 5a, with 4.5 mol% SG1 free nitroxide shown in Figure 5b and with 9.0 mol% SG1 free nitroxide shown in Figure 5c indicates the effect of free nitroxide on the molecular weight distribution clearly. Without free nitroxide, the PDI gradually increased as the initial acrylic acid concentration in the feed $f_{AA,0}$ increases.

The PDI rose to nearly 1.5 at $f_{AA,0}$ = 80 mol%. However, the PDI remained nearly constant in the range from 1.3 to 1.4 with increasing $f_{AA,0}$ when 4.5 mol% of free nitroxide was added with the only exception being the experiments for $f_{AA,0}$ = 80 mol% at relatively high conversions where the PDI increased to above 1.4. Thus, the free nitroxide plays a key role in maintaining a relatively narrow molecular weight distribution, especially at higher acrylic acid compositions. With 9.0 mol% SG1 free nitroxide relative to BlocBuilder®, molecular weight distributions were narrower with most PDI's below 1.3 and only started to rise at higher conversions as termination reactions became more common. Thus, using 9 mol% SG1 free nitroxide relative to BlocBuilder® noticeably improved the control over the molecular weight distribution. Figure 6 indicates the effect of increasing SG1 free nitroxide on the molecular weight distributions measured by gel permeation chromatography (GPC) from samples taken at various times. Table 3 details the molecular weight characterization for the various chromatograms shown in Figure 6.

The most interesting result from this styrene/acrylic acid copolymerization kinetic study was the ability to attain such relatively good control (as observed by the linear behavior up to conversions ~ 40% and PDIs < 1.5) at such high monomer feed concentrations. The monomer concentrations used were about twice that of previous studies for the same copolymerization system (50 wt% versus 21 wt% or 5-6 $mol{\cdot}L^{-1}$ versus 3 $mol{\cdot}L^{-1}$)[14]. The only difference between the two studies besides the concentration difference is the nature of the alkoxyamine used. Here, the more labile BlocBuilder® was used instead of MONAMS. Chauvin et al compared BlocBuilder® with MONAMS using styrene and n-butyl acrylate monomers[33]. Polymerizations using the tertiary radical forming BlocBuilder® were more controlled due to the higher homolysis rate of BlocBuilder® compared to the secondary radical forming MONAMS. The higher dissociation rate constant of BlocBuilder® allowed the production of an excess of free nitroxide required to regulate the polymerization. Thus, polymerizations using BlocBuilder® are promising and a strict comparison of BlocBuilder® to MONAMS at a fixed free nitroxide/initiator and monomer feed concentration should prove whether BlocBuilder® can indeed regulate polymerizations such as the acrylic acid/styrene system in concentrated solution more effectively. As noted by Chauvin et al.[33], careful consideration of heat transfer effects, monomer purification and temperature ramping protocol must also be considered. We are now starting heat transfer studies in jacketed reactors to examine the effect of monomer loading in more detail on styrene/acrylic acid controlled radical polymerization.

Another key point underlying all of the kinetic results and associated effects on molecular properties presented here is the stability of the SG1 and BlocBuilder® nitroxides to acrylic acid. Farcet et al. reported pH had a significant effect on polymerization rate and molecular weight control in miniemulsion conditions due to the degradation of the SG1 at low pH[43]. When a buffer was introduced to neutralize the system, SG1 stability was improved and the polymerizations were more controlled. A previous study of acrylic acid homopolymerization mediated by SG1 and initiated by MONAMS found a higher concentration of free nitroxide (9 mol% SG1 relative to MONAMS) was necessary to achieve a controlled polymerization compared to that of styrene/acrylic acid copolymerizations (4.5 mol% SG1 relative to MONAMS). Some of the additional SG1 free nitroxide employed for the acrylic acid homopolymerization could have likely been sacrificed to overcome the degradative side reactions. We are currently examining this issue by performing chain extension experiments as well as neutralizing the acrylic acid with a protecting group and then performing the nitroxide-mediated polymerization of the protected acrylate as a function of free nitroxide added.

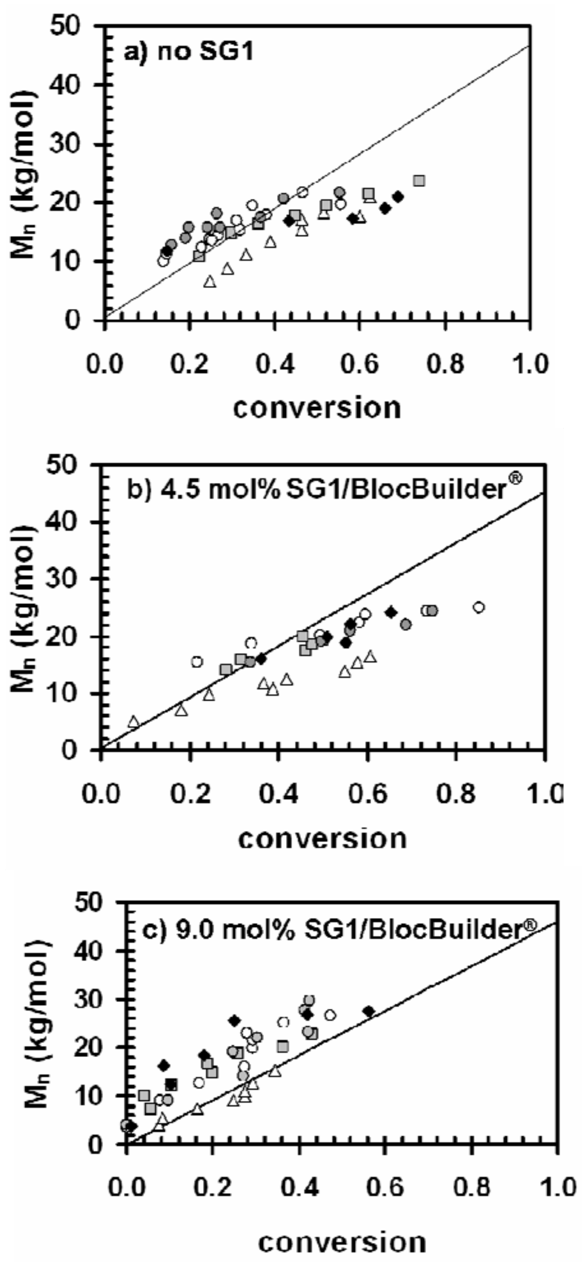

Figure 4: Number average molecular weight (M_n) measured using gel permeation chromatography (GPC) relative to poly(styrene) standards versus conversion for styrene (S)/acrylic acid (AA) random copolymers shown a) without any free SG1 nitroxide and b) with 4.5 mol% SG1 relative to BlocBuilder® nitroxide and c) with 9.0 mol% SG1 relative to BlocBuilder® nitroxide for various initial molar feed concentrations of AA. All syntheses were done at 120^{o}C with 50 wt% monomer solutions in 1,4-dioxane. The straight line indicates the theoretical M_n versus conversion. The initial monomer feed molar fraction of acrylic acid $f_{AA,0}$ indicated in the figure correspond to $f_{AA,0}$ = 0% (△), $f_{AA,0}$ = 20%, (□), $f_{AA,0}$ = 40% (○), $f_{AA,0}$ = 60% (◍) and $f_{AA,0}$ = 80%(♦).

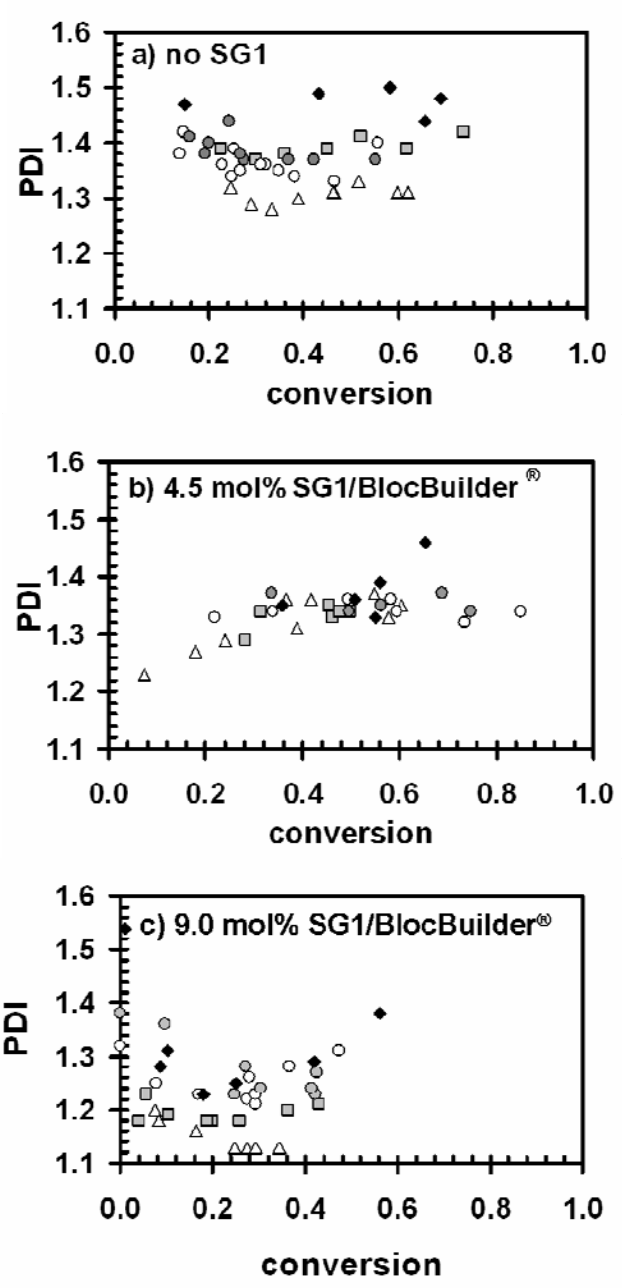

Figure 5: Polydispersity index (PDI) measured by gel permeation chromatography (GPC) relative to poly(styrene) standards versus conversion for styrene (S)-acrylic acid (AA) random copolymers synthesized with 50 wt% monomer solutions in 1,4-dioxane at 120^{o}C a) without any free SG1 nitroxide, b) with 4.5 mol% SG1 relative to BlocBuilder$^{®}$ nitroxide and c) with 9.0 mol% SG1 relative to BlocBuilder$^{®}$ nitroxide for various initial molar feed concentrations of AA. The initial monomer feed molar fraction of acrylic acid $f_{AA,0}$ indicated in the figure correspond to $f_{AA,0}$ = 0 mol% (△), $f_{AA,0}$ = 20 mol% (□), $f_{AA,0}$ = 40 mol% (○), $f_{AA,0}$ = 60 mol% (◍) and $f_{AA,0}$ = 80 mol% (♦).

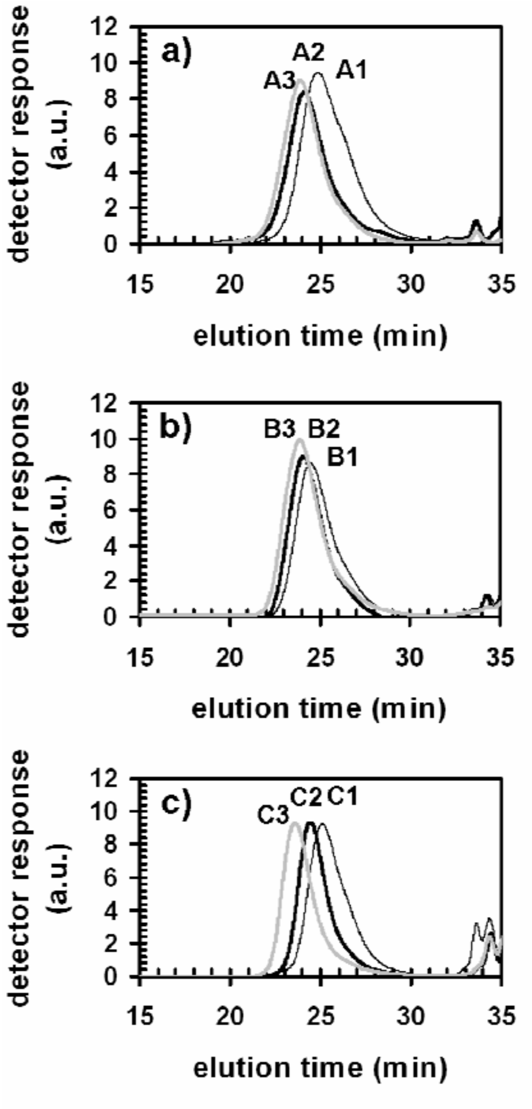

Figure 6: Gel permeation chromatograms (GPC) of styrene-ran-acrylic acid copolymers after polymerization at 120°C with 50 wt% monomer feed loadings in 1,4-dioxane for initial acrylic acid molar feed fractions $f_{AA,0}$ = 80 mol%. Each set of chromatograms corresponds to a different molar ratio of free SG1 nitroxide initially to BlocBuilder® initially (i.e. the r value = $[SG1]_0/[BlocBuilder^{®}]_0$). The set of chromatograms in a) refer to polymerizations with r = 0 (i.e. only BlocBuilder®). Note the relative broadness of the molecular weight distributions. With increasing free nitroxide as indicated by the set of chromatograms in b) with r = 0.045, the distributions became narrower and became even more narrow when r was increased to r = 0.09 as indicated by the set of chromatograms in c). The number average number average molecular weight M_n, weight average molecular weight M_w and polydispersity index (PDI = M_w/M_n) for the various chromatograms indicated are summarized in Table 3.

Copolymer Composition. If the propensity of a styrene monomer to add onto a styrene terminated radical chain is much greater than that for an acrylic acid monomer, the functional groups may not be present where they are desired. Thus, knowledge of the monomer sequence distribution as represented by the reactivity ratios is essential for assessing potential performance in the desired application. Previous studies examining the random free radical copolymerization of styrene with acrylic acid using MONAMS[14] and conventional initiators[44-48] are summarized in Table 4. Using the SG1/MONAMS mediating system and a similar temperature to that used in our experiments, Couvreur et al. reported reactivity ratios for AA (r_{AA}) and styrene (r_S) to be $r_{AA} = 0.27 \pm 0.07$ and $r_S = 0.72 \pm 0.04$[14]. With the samples taken at low conversions using BlocBuilder® as the unimolecular initiator with [SG1]/[BlocBuilder®] = 0.09 (see Table 5), Fineman-Ross[49] and Kelen-Tudos plots[50] were constructed to obtain approximate values for the reactivity ratios assuming a terminal model was valid for the copolymer chain reactivity[51]. Since we used a relatively small number of compositions to estimate reactivity ratios, biasing of data caused by the Fineman-Ross method linearization was expected to be more severe and we applied the Kelen-Tüdos method to estimate the reactivity ratios to be used for initial guesses of a non-linear least squares fit of the data. The latter method is expected to be the most statistically sound method to obtain the reactivity. The Kelen-Tüdos plot of the parameters η versus ξ reveal the reactivity ratios for r_1 and r_2 (monomer 1 = AA, monomer 2 = styrene) from the slope and intercept.

$$\eta = \left(r_1 + \frac{r_2}{\alpha} \right) \xi - \frac{r_2}{\alpha} \tag{4}$$

In Equation (4), the scaling parameter α is given by $\sqrt{H_{\min} H_{\max}}$ while η and ξ are derived from the linearized Fineman-Ross parameters G and H as indicated below in Equations (5) and (6).

$$\eta = \frac{G}{\alpha + H}; \ \xi = \frac{H}{\alpha + H} \tag{5}$$

$$G = \frac{f_1}{(1 - f_1)} \frac{(2F_1 - 1)}{F_1}; \ H = \left[\frac{f_1}{(1 - f_1)} \right]^2 \frac{(1 - F_1)}{F_1} \tag{6}$$

H_{min} and H_{max} correspond to the minimum and maximum values of H, respectively, determined from the data. After performing the Kelen-Tüdos fit of our data, the reactivity ratios were found to be $r_{AA} = 0.27$ and $r_S = 0.98$. Using the reactivity ratios determined by the Kelen-Tüdos as initial estimates, reactivity ratios using the non-linear least squares method (SigmaPlot 10.0 software) were $r_{AA} = 0.25 \pm 0.11$ and $r_S = 0.93 \pm 0.37$ which are in relatively good agreement with those reported by Couvreur et al[14]. Figure 7 shows the Mayo plot comparing the fit to the experimental data using non-linear least squares minimization along with the prediction of the Mayo-Lewis equation using the reactivity ratios reported by Couvreur et al.[14] The use of a different unimolecular initiator together with the concentrated solutions tended to not affect the reactivity ratios significantly compared to previous work using the same acrylic acid/styrene copolymerization system.

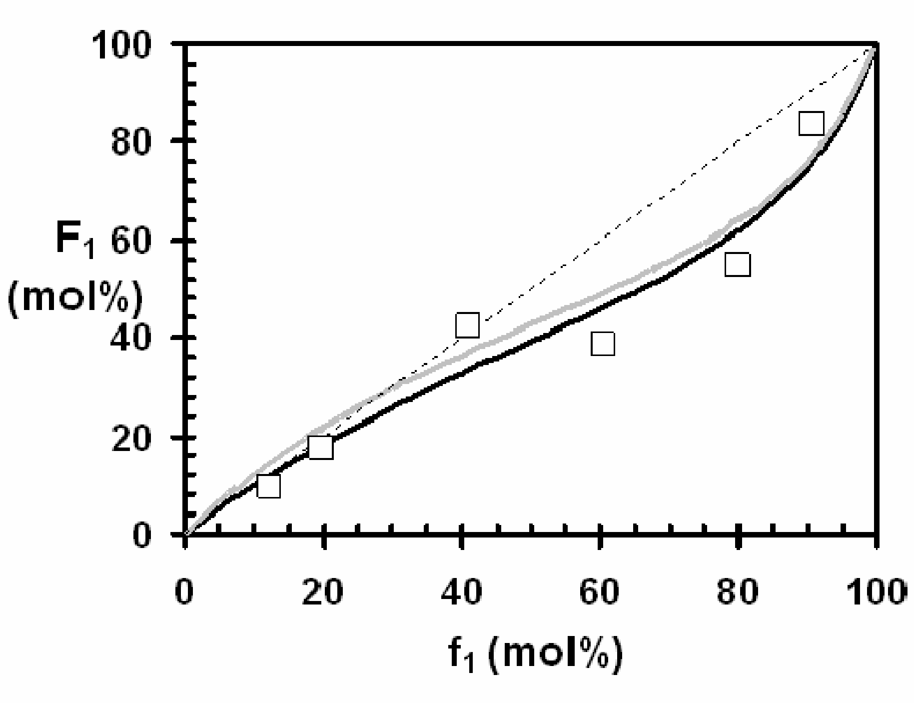

Figure 7: Composition of acrylic acid in the copolymer (F_{AA}) versus initial acrylic acid feed fraction ($f_{AA,0}$) for copolymerizations conducted with SG1 free ntiroxide plus BlocBuilder® unimolecular initiator only (open squares □) (9 mol% SG1/ BlocBuilder®). All copolymerizations were done in 50 wt% monomer solutions in 1,4-dioxane at 120°C. The dark solid line indicates predicted copolymer composition using the reactivity ratios determined from the experimental data with a non-linear least squares fit of the Mayo-Lewis equation (for acrylic acid $r_{AA} = 0.25\pm0.11$ and styrene $r_S = 0.93\pm0.37$) The grey solid line indicates the Mayo-Lewis equation plotted using the reactivity ratios calculated by Couvreur et al[14] for copolymerizations done with MONAMS unimolecular initiator and 4.5 mol% SG1/MONAMS at 120°C in 21 wt% monomer solutions in 1,4 dioxane ($r_{AA} = 0.27\pm0.07$, $r_S = 0.72\pm0.04$). The dashed line indicates where the copolymer composition is equal to the feed composition.

CONCLUSIONS

The effect of adding SG1 free nitroxide to the BlocBuilder® mediator on the nitroxide mediated polymerization of styrene/acrylic acid mixtures in terms of kinetics and copolymer composition was studied at 120°C in highly concentrated 1,4-dioxane solutions (~50 wt% monomer). With BlocBuilder® only, the polymerization rates were much more strongly affected by the composition of acrylic acid in the feed ($f_{AA,0}$). Polymerization rates were markedly faster and molecular weight distributions broadened with polydispersities ~ 1.5 at the highest initial acrylic acid feed fraction studied ($f_{AA,0}$ = 80 mol%). By adding 4.5 mol% SG1 free nitroxide relative to BlocBuilder®, polymerization rates were not as strongly affected by $f_{AA,0}$ and polydispersities remained ~ 1.3-1.4 regardless of feed composition with the only exception at high conversions with the highest $f_{AA,0}$ studied. Values of k_pK from experiments using 4.5 mol% SG1/BlocBuilder® at 120°C were in good agreement with previous studies except at the highest $f_{AA,0}$ studied where the observed exotherms due to the high monomer loading may have altered the propagation and equilibrium rate constants. Further, estimates of k_pK could be affected by degradative side reactions of SG1 caused by the acrylic acid. When using 9 mol% SG1/BlocBuilder®, exotherms were negligible at all feed compositions and k_pK values varied between that of pure styrene and acrylic acid hompolymerizations conducted at 120°C. Copolymer reactivity ratios estimated from experiments with 9 mol% SG1/BlocBuilder® in the concentrated solutions examined here yielded $r_{AA} = 0.27 \pm 0.11$ and $r_S = 0.93 \pm 0.37$ by non-linear least squares fitting. The reactivity ratios calculated here are in relatively good agreement with those reported in previous studies using nitroxide mediated polymerization by SG1/MONAMS[14] and conventional free radical polymerizations[44-48].

ACKNOWLEDGMENT

This work was supported by the Canada Foundation for Innovation (CFI) New Opportunities Fund and NSERC Discovery Grant. BL acknowledges scholarship support from the Dept. of Chemical Engineering, McGill University. We also thank Noah Macy of Arkema, Inc. for aid in obtaining the BlocBuilder® unimolecular initiator and SG1 mediator used in this work.

FIGURE CAPTIONS

Figure 1: Structures of various alkoxyamine mediators and unimolecular initiators used for nitroxide-mediated 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); c) 2-[N-*tert*-Butyl-2,2-dimethylpropyl)aminoxy] propionic acid (BlocBuilder®).

Figure 2: Scaled conversion ($\ln(1-x)^{-1}$) (x = monomer conversion) versus time for styrene-acrylic acid (S-r-AA) random copolymerizations of various feed compositions done in 50 wt% 1,4-dioxane solution at 120°C a) without any free SG1 nitroxide, b) with 4.5 mol% SG1 relative to BlocBuilder® and c) with 9.0 mol% SG1 relative to BlocBuilder®. The solid lines are linear fits to the data taken at early times used to calculate apparent rate constants $k_p[P^\bullet]$ where k_p is the propagation rate constant and $[P^\bullet]$ is the concentration of propagating macro-radicals. The initial monomer feed molar fraction of acrylic acid $f_{AA,0}$ indicated for each set in the figure correspond to $f_{AA,0}$ = 0 mol% (△), $f_{AA,0}$ = 20 mol% (■), $f_{AA,0}$ = 40 mol% (○), $f_{AA,0}$ = 60 mol% (●) and $f_{AA,0}$ = 80 mol%(♦).

Figure 3: Product of propagation rate constant k_p and equilibrium constant K (k_pK) versus % acrylic acid molar feed fraction $f_{AA,0}$ for styrene/acrylic acid compositions copolymerized at 120°C in 50 wt% 1,4-dioxane solution as a function of added SG1 free nitroxide (4.5 mol% SG1 relative to BlocBuilder® indicated by filled diamonds (♦) and 9.0 mol% SG1 relative to BlocBuilder® indicated by open squares (□)). The dashed lines indicate the k_pK value for pure styrene ($k_pK_{styrene}$) at 120°C[15] and the range of k_pK values for acrylic acid (k_pK_{AA}) in the hatched area corresponds to the literature values found for pure acrylic acid feeds at 120°C[13].

Figure 4: Number average molecular weight (M_n) measured using gel permeation chromatography (GPC) relative to poly(styrene) standards versus conversion for styrene (S)/acrylic acid (AA) random copolymers shown a) without any free SG1 nitroxide and b) with 4.5 mol% SG1 relative to BlocBuilder® nitroxide and c) with 9.0 mol% SG1 relative to BlocBuilder® nitroxide for various initial molar feed concentrations of AA. All syntheses were done at 120^{o}C with 50 wt% monomer solutions in 1,4-dioxane. The straight line indicates the theoretical M_n versus conversion. The initial monomer feed molar fraction of acrylic acid $f_{AA,0}$ indicated in the figure correspond to $f_{AA,0}$ = 0 mol% (△), $f_{AA,0}$ = 20 mol %, (□), $f_{AA,0}$ = 40 mol% (○), $f_{AA,0}$ = 60 mol% (◍) and $f_{AA,0}$ = 80 mol%(♦).

Figure 5: Polydispersity index (PDI) measured by gel permeation chromatography (GPC) relative to poly(styrene) standards versus conversion for styrene (S)-acrylic acid (AA) random copolymers synthesized with 50 wt% monomer solutions in 1,4-dioxane at 120^{o}C a) without any free SG1 nitroxide, b) with 4.5 mol% SG1 relative to BlocBuilder® nitroxide and c) with 9.0 mol% SG1 relative to BlocBuilder® nitroxide for various initial molar feed concentrations of AA. The initial monomer feed molar fraction of acrylic acid $f_{AA,0}$ indicated in the figure correspond to $f_{AA,0}$ = 0 mol% (△), $f_{AA,0}$ = 20 mol% (□), $f_{AA,0}$ = 40 mol% (○), $f_{AA,0}$ = 60 mol% (◍) and $f_{AA,0}$ = 80 mol% (♦).

Figure 6: Gel permeation chromatograms (GPC) of styrene-ran-acrylic acid copolymers after polymerization at 120^{o}C with 50 wt% monomer feed loadings in 1,4-dioxane for initial acrylic acid molar feed fractions $f_{AA,0}$ = 80 mol%. Each set of chromatograms corresponds to a different molar ratio of free SG1 nitroxide initially to BlocBuilder® initially (i.e. the r value = $[SG1]_0/[BlocBuilder^{®}]_0$). The set of chromatograms in a) refer to polymerizations with r = 0 (i.e. only BlocBuilder®). Note the relative broadness of the molecular weight distributions. With increasing free nitroxide as indicated by the set of chromatograms in b) with r = 0.045, the distributions became narrower and became even more narrow when r was increased to r = 0.09 as indicated by the set of chromatograms in c). The number

average number average molecular weight M_n, weight average molecular weight M_w and polydispersity index (PDI = M_w/M_n) for the various chromatograms indicated are summarized in Table 3.

Figure 7: Composition of acrylic acid in the copolymer (F_{AA}) versus initial acrylic acid feed fraction ($f_{AA,0}$) for copolymerizations conducted with SG1 free ntiroxide plus BlocBuilder® unimolecular initiator only (open squares □) (9 mol% SG1/ BlocBuilder®). All copolymerizations were done in 50 wt% monomer solutions in 1,4-dioxane at 120°C. The dark solid line indicates predicted copolymer composition using the reactivity ratios determined from the experimental data with a non-linear least squares fit of the Mayo-Lewis equation (for acrylic acid r_{AA} = 0.25±0.11 and styrene r_S = 0.93±0.37) The grey solid line indicates the Mayo-Lewis equation plotted using the reactivity ratios calculated by Couvreur et al[14] for copolymerizations done with MONAMS unimolecular initiator and 4.5 mol% SG1/MONAMS at 120°C in 21 wt% monomer solutions in 1,4 dioxane (r_{AA} = 0.27±0.07, r_S = 0.72±0.04). The dashed line indicates where the copolymer composition is equal to the feed composition.

Table 1: Experimental Conditions for Acrylic Acid (AA)/Styrene (S) Copolymerizations at 120°C in 1,4-Dioxane with BlocBuilder® only and with Additional SG1 Free Nitroxide

Experiment ID[a)]	[BlocBuilder®]$_0$ (mol·L^{-1})	[SG1]$_0$ (mol·L^{-1})	r[b)]	[S]$_0$ (mol·L^{-1})	[AA]$_0$ (mol·L^{-1})	[solvent]$_0$ (mol·L^{-1})
S-r-AA-50-0-0	0.011	-	-	4.6	0.0	5.5
S-r-AA-50-20-0	0.011	-	-	4.1	1.0	5.4
S-r-AA-50-40-0	0.011	-	-	3.3	2.2	5.5
S-r-AA-50-60-0	0.011	-	-	2.4	3.5	5.7
S-r-AA-50-80-0	0.012	-	-	1.2	5.2	5.8
S-r-AA-50-0-4.5	0.011	5×10^{-4}	0.045	4.6	0.0	5.5
S-r-AA-50-20-4.5	0.011	5×10^{-4}	0.045	4.0	1.0	5.5
S-r-AA-50-40-4.5	0.011	5×10^{-4}	0.045	3.2	2.2	5.6
S-r-AA-50-60-4.5	0.011	5×10^{-4}	0.045	2.4	3.5	5.7
S-r-AA-50-80-4.5	0.011	5×10^{-4}	0.045	1.3	5.2	5.8
S-r-AA-50-0-9.0	0.011	1×10^{-3}	0.09	4.7	0.0	5.5
S-r-AA-50-20-9.0	0.011	1×10^{-3}	0.09	4.0	1.0	5.6
S-r-AA-50-40-9.0	0.011	1×10^{-3}	0.09	3.3	2.2	5.6
S-r-AA-50-60-9.0	0.011	1×10^{-3}	0.09	2.4	3.6	5.7
S-r-AA-50-80-9.0	0.011	1×10^{-3}	0.09	1.3	5.2	5.8

[a] Experiment ID is given by the following notation S-r-AA-XX-YY-ZZ where XX represents the monomer feed loading in the solution in wt%, YY represents the % molar fraction of acrylic acid in the monomer feed and ZZ represents the % ratio of initial moles of SG1 free nitroxide mediator relative to initial moles of BlocBuilder® unimolecular initiator which is defined by the r ratio given in the table footnote b).

[b] r = ratio of initial moles of SG1 to initial moles of BlocBuilder® = [SG1]$_0$/[BlocBuilder®]$_0$.

Table 2: Kinetic Parameters for Various Feed Compositions of Acrylic Acid (AA) with Styrene (S) at 120°C with BlocBuilder® only and with additional SG1 Free Nitroxide for Monomer Feed Concentrations Equal to 50 wt%.

$f_{AA,0}$ [a)]	BlocBuilder® only	SG1/ BlocBuilder® (r = 0.045[b])		SG1/ BlocBuilder® (r = 0.090)	
	$k_p[P^\bullet]$ (x 10^4 s^{-1})	$k_p[P^\bullet]$ (x 10^4 s^{-1})	k_pK (x 10^6 s^{-1})	$k_p[P^\bullet]$ (x 10^4 s^{-1})	k_pK (x 10^6 s^{-1})
0	1.3 ± 0.2	1.1 ± 0.1	4.9 ± 0.4	0.50 ± 0.06	4.5 ± 0.6
20	2.8 ± 0.2	1.2 ± 0.2	5.6 ± 0.7	0.75 ± 0.08	6.7 ± 0.7
40	3.1 ± 0.3	2.3 ± 0.2	10.0 ± 0.7	0.74 ± 0.09	6.6 ± 0.8
60	5.0 ± 0.8	2.7 ± 0.1	12.0 ± 0.5	1.0 ± 0.1	9.1 ± 1.2
80	11.1 ± 0.1	3.9 ± 0.9	17.0 ± 4	1.0 ± 0.2	9.5 ± 1.9

[a] $f_{AA,0}$ is defined as the % molar fraction of acrylic acid in the initial feed.

[b] r = ratio of initial moles of SG1 to initial moles of BlocBuilder® = $[SG1]_0$/[BlocBuilder®]$_0$.

Kinetic parameters determined from initial slopes $k_p[P^\bullet]$ of semi-logarithmic plots of $\ln[(1-x)^{-1}]$ versus time where x = conversion of monomer, k_p = propagation rate constant and $[P^\bullet]$ is the concentration of growing chains. K is the equilibrium constant defined in Equation [1]. Error bars are derived from the standard error of the slopes ($k_p[P^\bullet]$) from the linear fits of $\ln[(1-x)^{-1}]$ versus time.

Table 3: Molecular Weight Distribution Characteristics of Styrene-ran-Acrylic Acid Copolymers at Various Ratios of SG1 Free Nitroxide/BlocBuilder® For Gel Permeation Chromatograms Indicated in Figure 6 (Initial Monomer Molar Feed Fractions = 80 mol% Acrylic Acid).

r[a)]	Sample ID[b)]	$t_{polymerization}$ (min)[c)]	Conversion X	M_n[d)] (kg/mol)	M_w[d)] (kg/mol)	M_w/M_n[d)]
0	A1	3	0.15	11.8	17.2	1.47
0	A2	12	0.58	17.4	26.2	1.50
0	A3	18	0.69	21.1	31.3	1.48
0.045	B1	10	0.36	16.0	21.7	1.35
0.045	B2	20	0.51	19.9	27.1	1.36
0.045	B3	30	0.56	22.2	30.8	1.39
0.09	C1	15	0.10	12.5	16.4	1.31
0.09	C2	45	0.18	18.4	22.6	1.23
0.09	C3	75	0.42	26.8	34.7	1.29

[a] r = molar ratio of SG1 nitroxide initially added to that of BlocBuilder® = $[SG1]_0/[BlocBuilder^{®}]_0$

[b] Sample ID corresponds to the labeling of each chromatogram shown in Figure 6.

[c] All polymerizations were done at 120°C in 50 wt% monomer feed concentrations in 1,4-dioxane solvent with acrylic acid molar feed fractions in the monomer feed mixture corresponding to 80 mol% acrylic acid.

[d] Number average molecular weight M_n, weight average molecular weight M_w and polydispersity index = M_w/M_n were determined using gel permeation chromatography (GPC) in tetrahydrofuran (THF) at 40°C relative to poly(styrene) standards. The copolymer molecular weights were measured after derivatization of acrylic acid groups with trimethylsilyldiazomethane to make the copolymers soluble in THF.

Table 4: Comparison of Reactivity Ratios Obtained for Styrene/Acrylic Acid Random Copolymers

Reference	r_{AA}	r_S	T (^oC)	solvent	initiator
Chapin et al.[44]	0.15	0.25	60	bulk	benzoyl peroxide (BPO)
Toppet et al.[45]	0.13	0.30	60	benzene	azobis isobutyronitrile (AIBN)
	0.05	1.60	60	dimethyl formamide (DMF)	AIBN
Kerber[46]	0.07	0.25	50	bulk	AIBN
	0.13	0.75	50	1,4-dioxane	AIBN
	0.15	1.03	50	DMF	AIBN
Ryabanov[47]	0.05	0.25	45	bulk	BPO
	0.08	1.1	45	DMF	BPO
Wang & Poehlein[48]	0.13	0.38	50	bulk	AIBN
Couvreur et al.[14]	0.27±0.07	0.72±0.04	120	1,4-dioxane	MONAMS[a]/SG1[b]
this work	0.25±0.11[d]	0.93±0.37[d]	120	1,4-dioxane	BlocBuilder®/SG1 [c]

[a] MONAMS = N-*tert*-Butyl-N-1-diethylphosphono-2,2-dimethylpropyl-O-1-methoxycarbonylethylhydroxylamine

[b] SG1 = N-tert-butyl-N-[1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide

[c] BlocBuilder® = 2-[N-*tert*-Butyl-2,2-dimethylpropyl)aminoxy] propionic acid

[d] reactivity ratios determined by non-linear least squares regression of the Mayo-Lewis equation

Table 5: Characterization of Acrylic Acid/Styrene Random Copolymers Synthesized at 120°C in 50 wt% Monomer Solution in 1,4 Dioxane using 9 mol% SG1/BlocBuilder for Determination of Copolymer Reactivity Ratios

$f_{AA,0}$[a]	F_{AA}[b]	Conversion (X)[c]	M_n (kg/mol)[d]	M_w (kg/mol)[d]	M_w/M_n[d]
12.2	9.6	0.06	3.5	4.3	1.25
19.9	17.8	0.13	3.4	4.4	1.28
41.1	42.3	0.10	4.9	6.1	1.25
60.3	38.6	0.19	6.2	7.8	1.26
80.0	54.9	0.24	8.0	9.9	1.23
90.5	83.3	0.18	5.4	6.9	1.28

[a] $f_{AA,0}$ is the initial % molar feed fraction of acrylic acid

[b] F_{AA} is the % molar fraction of acrylic acid in the copolymer determined using ^{1}H nuclear magnetic resonance (NMR).

[c] X is the conversion of the copolymer determined by gravimetry.

[d] Number-average (M_n), weight-average (M_w) and polydispersity index (M_w/M_n) determined after methylation of acrylic acid units in the copolymer by trimethylsilyldiazomethane followed by gel permeation chromatography (GPC) relative to poly(styrene) standards in tetrahydrofuran at 40°C.

Supporting Information Available: Sample ^{1}H NMR spectra and raw data to determine copolymer compositions from the spectra are shown along with Kelen-Tüdos plots used for providing initial estimates of the copolymer reactivity ratios. This material is available free of charge via the Internet at http://pubs.acs.org.

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Styrene/Acrylic Acid Random Copolymers Synthesized by Nitroxide Mediated Polymerization: Effect of Free Nitroxide on Kinetics and Copolymer Composition

Benoît Lessard, Scott Schmidt and Milan Marić