

Effect of Acid Protecting Group on “Livingness” of Poly(acrylic acid-*ran*-styrene) Random Copolymer Macroinitiators for Nitroxide-Mediated Polymerization of Styrene

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ABSTRACT: Poly(acrylic acid-*ran*-styrene) (P(AA-*r*-S)) and poly(*tert*-butyl acrylate-*ran*-styrene) (P(*t*BuA-*r*-S)) random copolymers previously made with different molar ratios (0, 4.5 and 9 mol%) of additional free nitroxide mediator, N-*tert*-butyl-N-[1'-diethylphosphono-2,2'-dimethylpropyl] nitroxide (SG1), relative to 2-[N-*tert*-butyl-2,2-(dimethylpropyl)aminoxy]propionic acid (BlocBuilder®) alkoxyamine unimolecular initiator were used as macroinitiators for styrene chain extension. The reinitiating experiments were performed in bulk at 115 °C when using P(*t*BuA-*r*-S) macroinitiators or 30-50 wt% dioxane solution at 120 °C when using P(AA-*r*-S) macroinitiators. The P(*t*BuA-*r*-S) containing macroinitiators (number average molecular weight $\bar{M}_n = 13.4\text{--}25.8 \text{ kg}\cdot\text{mol}^{-1}$) with polydispersities $\bar{M}_w/\bar{M}_n = 1.13\text{--}1.57$ were capable of initiating chains extended with styrene as indicated by monomodal and narrow molecular weight distributions with $\bar{M}_n$'s = 34.6-66.3 $\text{kg}\cdot\text{mol}^{-1}$ and $\bar{M}_w/\bar{M}_n$'s ranging from 1.24-1.39. Unprotected P(AA-*ran*-S) acrylic acid containing macroinitiators ($\bar{M}_n = 19.7\text{--}28.8 \text{ kg}\cdot\text{mol}^{-1}$) with $\bar{M}_w/\bar{M}_n$'s ranging from 1.34-1.48 also initiated chain extensions with styrene but tended to have much higher $\bar{M}_w/\bar{M}_n$'s of 1.50-2.47. In some cases, dead chains that failed to re-initiate were clearly observed from the gel permeation chromatograms. The acrylic acid likely degraded the alkoxyamine as suggested by previous literature, reducing the SG1-active chain end concentration and thereby decreasing the control of the molecular weight distribution. Based on these findings, a more desirable route towards higher molecular weight poly(acrylic acid) containing block copolymers by nitroxide-mediated polymerization is likely done by polymerization of the protected acrylic acid followed by suitable deprotection.

Introduction

Recent advances in controlled free radical polymerization offer robust and versatile synthetic routes to well-defined, low polydispersity polymers¹⁻⁵ for applications ranging from next-generation separations media,^{6,7} controlled release vehicles,⁸⁻¹⁰ catalyst supports,¹¹ nanoreactors,¹² sensors^{13,14} and hydrogen storage systems.¹⁵ Such polymers have traditionally been synthesized via techniques such as ionic polymerization.^{16,17} Controlled free radical polymerization is attractive because it has been found to exhibit similar control of chain length but it does not require the intensive solvent purification or air-free transfers which are mandatory for ionic polymerization. Furthermore, free radical polymerization opens possibilities for the polymerization of monomers that were unsuitable candidates for ionic polymerization¹⁸.

Acrylic acid (AA) is a functional monomer that cannot be polymerized directly via ionic polymerization due to its tendency to terminate propagating chain ends and must be protected by *tert*-butyl or trimethylsilyl protecting groups during polymerization. However, AA can be polymerized directly by conventional free radical polymerization and has been polymerized by controlled radical polymerization techniques such as reversible addition fragmentation transfer (RAFT)¹⁹⁻²² and with the development of alkoxyamine initiators based on the so-called SG1 free nitroxides such as MONAMS and BlocBuilder® (Scheme 1), nitroxide-mediated polymerization (NMP).²³⁻²⁸ Polymerizations with SG1-related initiators can be done at much lower temperatures (as low as 90 °C)²⁹⁻³² compared to the TEMPO-based family of nitroxides originally used to control styrene polymerizations. With the acyclic β -phosphonylated SG1 nitroxide family of alkoxyamines, even controlled methacrylate polymerizations become possible under certain conditions.³³⁻³⁸ For example, Dire et al copolymerized methacrylic acid (MAA) with a small amount of styrene co-monomer (S) in 1,4 dioxane solvent (~ 8 mol% styrene in the monomer feed) with 10 mol% SG1/BlocBuilder® at 73-83 °C for target $\bar{M}_n \approx 10 \text{ kg} \cdot \text{mol}^{-1}$ resulting in linear increases in $\bar{M}_n$ with conversion and $\bar{M}_w/\bar{M}_n$ as low as 1.2.³³ Chain extension of a resultant poly(MAA-*r*-S) macroinitiator with a second batch of styrene cleanly produced a diblock copolymer with $\bar{M}_n = 17.7 \text{ kg} \cdot \text{mol}^{-1}$ with $\bar{M}_w/\bar{M}_n = 1.12$. In miniemulsion conditions, the water solubility of the

carboxylic acid functional BlocBuilder[®] when neutralized enabled its use as an initiator for n-butyl acrylate and styrene polymerizations using 0-2.7 mol% SG1 relative to BlocBuilder[®] at 120 °C and resulted in linear increases in $\bar{M}_n$ versus conversion with $\bar{M}_n \approx 30 \text{ kg} \cdot \text{mol}^{-1}$ and $\bar{M}_w/\bar{M}_n$ ranging from 1.2-1.4.²⁵

Despite the versatility and potency of the SG1-derived BlocBuilder[®], the sensitivity of the SG1 free nitroxide towards strong acids such as acrylic acid may make it problematic in certain situations. Our group^{28,39} and others^{23,24} have found that more free nitroxide was typically required for the NMP of AA or AA mixtures with styrene compared to monomers such as styrene, *tert*-butyl acrylate (*t*BuA) and n-butyl acrylate. This was needed to compensate for the SG1 consumed in degradative side reactions with the monomer⁴⁰ and to control the exotherms associated with the high propagation rate constant of AA²³. Also, characterization of *t*BuA containing copolymers with other organo-soluble monomers may in some cases be easier than feed mixtures of AA/organo-soluble monomers. Rather than polymerizing AA directly by NMP it may be more facile to first polymerize *t*BuA followed by cleavage of the protecting group to yield AA functional groups as is the case with atom transfer radical polymerization (ATRP)^{41,42}.

We previously studied *t*BuA/S and AA/S random copolymerizations using 2-[N-*tert*-butyl-2,2-(dimethylpropyl)aminoxy] propionic acid as the unimolecular initiator (BlocBuilder[®]) and N-*tert*-butyl-N-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (SG1) as the free nitroxide^{28,39}. We found that *t*BuA/S copolymerizations exhibited pseudo-“living” behavior (eg. linear increase of number average molecular weight versus conversion and narrow molecular weight distributions with polydispersities < 1.4) up to conversions ~ 50% with the addition of 4.5 mol% SG1 free nitroxide/BlocBuilder[®] whereas the acrylic acid/styrene copolymerizations required 9 mol% SG1/BlocBuilder[®] to exhibit the same pseudo-“living” behavior. We suspected that the degradation of the SG1 by acrylic acid during copolymerization affects the ability to re-initiate the copolymer in order to attach a second block. This has enormous implications, as the molecular weight distribution and compositional heterogeneity are key design factors for improved amphiphilic macromolecular

surfactants for emulsion polymerization^{27,43} or for copolymers with optimal interfacial activity as compatibilizers for polymer blends⁴⁴⁻⁴⁶. We thus tested the “livingness” of the AA/S and *t*BuA/S random copolymers previously prepared by performing chain extensions with styrene. In particular, we examined the effect of added free nitroxide used to make the macroinitiator and the composition of the macroinitiator on the ability to re-initiate a second batch of monomer as observed by changes in the molecular weight distribution using gel permeation chromatography (GPC). The results of the following study will indicate whether direct acrylic acid polymerization and/or copolymerization is as advantageous using NMP as originally anticipated and will attempt to answer whether it may actually be better to obtain AA containing copolymers via a *t*BuA containing precursor.

Experimental Section

Materials. Styrene (99%), basic alumina (Brockmann, Type 1, 150 mesh), (trimethylsilyl)diazomethane (2.0M solution in hexane) (95%), trifluoroacetic acid 2.0 M (99.5%) and calcium hydride (90-95% reagent grade) were all purchased from Aldrich while methanol (99.8%), tetrahydrofuran (99.5%), dioxane (99.5%) and methylene chloride (99.5%) were obtained from Fisher Scientific. The styrene was purified by passing through a column of basic alumina mixed with 5 wt% calcium hydride and then was stored in a sealed flask under a head of nitrogen in a refrigerator until needed. The poly(*tert*-butyl acrylate-*ran*-styrene) (P*t*BuA-*r*-S)) and poly(acrylic acid-*ran*-styrene) (P(AA-*r*-S)) random copolymer macroinitiators were previously synthesized using nitroxide mediated polymerization and the procedure to make the macroinitiators is detailed elsewhere^{28,39}.

Synthesis of Poly(*tert*-butyl acrylate-*ran*-styrene)-Poly(styrene) (P(*t*BuA-*r*-S)-PS) Diblock Copolymers. All the syntheses were performed in a 100 mL three neck round bottom glass flask. The reactor was equipped with a condenser connected to a chiller, a thermal well with a temperature probe and a magnetic Teflon-coated stir bar. The flask was mounted inside a heating mantle that was secured to a stirrer. A specific formulation using a given P(*t*BuA-*r*-S) macroinitiator and styrene monomer is shown as an example (Experiment TA6 in Tables 1 and 2). To the reactor was added 1.5 g (0.08 mmol)

of macroinitiator (number average molecular weight $\overline{M}_n = 19.6 \text{ kg}\cdot\text{mol}^{-1}$, polydispersity index = $\overline{M}_w/\overline{M}_n = 1.15$, molar fraction of *tert*-butyl acrylate in the copolymer $F_{t\text{BuA}} = 0.36$) along with 4.0 g (0.038 mol) of previously purified styrene by syringe and the contents were mixed with a magnetic stir bar. The macroinitiators were all slightly different in molecular weight and therefore recipes were altered to ensure that the target number average degree of polymerization ($\overline{M}_n$) of the second styrenic block was approximately equal to 500 in each case. All characteristics of the other P(*t*BuA-*r*-S) macroinitiators as well as the recipes are found in Tables 1 and 2. After adding the macroinitiator and styrene to the reactor, the flask was then sealed with a rubber septum. The thermocouple was connected to a controller and the condenser's chilling unit (Neslab 740) was filled with a 50% v/v glycol/water mixture and set to 5 °C to condense any vapors generated during the experiment. An ultra-pure nitrogen flow was used to purge the system during monomer injection, as well as during 15 minutes post-injection, at room temperature. The reactor was then heated to 115 °C at a rate of roughly 10 °C·min⁻¹ while maintaining a nitrogen purge. The start of the reaction ($t = 0$) was considered as the time when the reactor temperature reached 110 °C. Samples were taken with a syringe periodically until the samples became too viscous to withdraw. When the samples became too viscous, heating to the reactor was then stopped. For the particular example given, the polymerization was stopped after 11 minutes. All samples were precipitated into methanol. The samples were left to settle for several hours, then decanted and dried overnight in a vacuum oven at 70 °C to remove any solvent or un-reacted monomer. The conversion of the second styrene block was nearly 30% with diblock copolymer yield of about 2.8 g (51 %). The diblock $\overline{M}_n$ was equal to 35.6 kg·mol⁻¹ with $\overline{M}_w/\overline{M}_n = 1.24$ according to GPC calibrated with linear poly(styrene) standards in THF while the composition was $F_{t\text{BuA}} = 0.29$ according to ¹H NMR in CDCl₃. The molecular weight characteristics of all samples taken at various times from the rest of the styrene chain extensions from P(*t*BuA-*r*-S) macroinitiators is shown in Table 3.

Synthesis of Poly(Acrylic Acid-*ran*-Styrene)-Poly(Styrene) (P(AA-*r*-S)-PS) Diblock Copolymers.

The synthesis of the series of P(AA-*r*-S)-PS diblocks made with the various P(AA-*r*-S) macroinitiators (see Table 1 for formulations) was performed in the same reactor, apparatus and procedure as described

in the previous section for P(*t*BuA-*r*-S)-PS diblocks. When polymerizing the styrene from the P(AA-*r*-S) macroinitiator, the polymerization was performed in 30 or 50 wt% 1,4 dioxane solution rather than in bulk in order to duplicate the conditions under which the P(AA-*r*-S) macroinitiator was made. Formulation AA5 shown in Table 4 is given as an example below. To the reactor was added 5.4 g of 1,4 dioxane along with 1.5 g (0.075 mmol) of P(AA-*r*-S) macroinitiator ($\bar{M}_n = 20.0 \text{ kg}\cdot\text{mol}^{-1}$, $\bar{M}_w/\bar{M}_n = 1.35$, acrylic acid composition in the copolymer $F_{AA} = 0.50$) with stirring. The reactor was sealed and then 3.9 g (0.038 mol) of styrene was added via syringe. After bubbling nitrogen for 30 minutes after addition of the reagents at room temperature, heating at about $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ to a set-point of $120 \text{ }^\circ\text{C}$ was started. Similar to the P(*t*BuA-*r*-PS)-PS experiments, samples were drawn periodically with a syringe but were then precipitated in hexane to obtain the crude polymer. The samples were then dried overnight in a vacuum oven at $70 \text{ }^\circ\text{C}$ to remove any solvent or non-reacted monomer. When the reaction medium became too viscous to remove samples by syringe, the polymerization was stopped. For the specific example, polymerization was stopped after 60 minutes and heating was stopped. After polymerization and drying, about 20 % of the styrene fed for the second block was converted, giving a yield of 2.4 g (44 %) of the P(AA-*r*-S)-PS product. The diblock copolymer had $\bar{M}_n = 30.8 \text{ kg}\cdot\text{mol}^{-1}$, $\bar{M}_w/\bar{M}_n = 1.50$ according to GPC in THF calibrated with linear poly(styrene) standards after suitable methylation of the acrylic acid units (see Characterization section for full details) and the copolymer composition was $F_{AA} = 0.39$ according to ^1H NMR measurements in CDCl_3 after methylation of the acrylic acid units. Table 5 summarizes the molecular weight data for all samples taken at various times from the rest of the P(AA-*r*-S) macroinitiators.

General Procedure for Conversion of Poly(*tert*-butyl acrylate) (PtBuA) to Poly(acrylic acid) (PAA) and Poly(*tert*-butyl acrylate)-*b*-Poly(styrene) (PtBuA-PS) to Poly(acrylic acid)-*b*-Poly(styrene) (PAA-PS). This procedure was performed in three different experiments termed SA1, SA2 and SA3 (see Table 6) as follows with the purpose of converting *tert*-butyl acrylate units in a segmented PS-PtBuA diblock to acrylic acid units by deprotection with trifluoroacetic acid (TFA). A 250-mL glass

round bottom flask was cleaned, dried and equipped with a stir bar and placed on a stir plate. As an example, the flask was filled with PtBuA-PS diblock (entry SA1 with $\square = 78.8 \text{ kg}\cdot\text{mol}^{-1}$, $\square = 1.47$; 1.3 g, 2.85 mmol of *tert*-butyl ester) followed by 45 mL of dichloromethane. The mixture was stirred until the polymer was completely in solution, which took approximately 10 minutes at ambient temperature. Then, 3.03 mL of TFA (4.6 g, 40.22 mmol, 14.2 equivalents excess to the *tert*-butyl ester) was added. The flask was sealed and the solution was stirred at room temperature overnight at room temperature. The flask was then purged with ultra pure nitrogen for 8 h to remove the dichloromethane and the excess TFA. The resulting polymer was glassy and was slightly yellow. The product was then dried under vacuum for 36 h at approximately 60 °C. The yield of the dry PS-PAA diblock copolymer was 1.30 g (74 %) and the sample was analyzed using GPC and ^1H NMR. The acrylic acid containing polymers were methylated using (trimethylsilyl)diazomethane to convert the acrylic acid groups to methyl acrylate groups, thereby allowing analysis by organic phase GPC using tetrahydrofuran (THF). This was done to check for any possible changes in molecular weight distribution after cleavage of the *tert*-butyl protecting groups. After methylation, the resulting PAA-PS diblock copolymer had $\square = 48.6 \text{ kg}\cdot\text{mol}^{-1}$ and $\square = 1.54$. Note that the $\square$'s were converted from PS standards using literature values of the Mark-Houwink coefficients for poly(methyl acrylate)⁴⁷. Adding the PAA-PS diblock polymer to a vial filled with distilled water allowed a solubility test. The sample was water-soluble, suggesting a high degree of conversion of PtBuA to PAA. The conversion to PAA was confirmed for all cases using ^1H NMR in deuterated acetone. The resonances corresponding to the *tert*-butyl group peak at $\delta = 1.3\text{-}1.5 \text{ ppm}$ which was present in the PtBuA sample was not found in the resulting PAA product confirming that the conversion was essentially complete. The ^1H NMR of the methylated blocks gave the following chemical shifts for the protons on the acrylic repeat units: $\delta = 1.7\text{-}1.9 \text{ ppm}$ (br, CH_2 of the polymer backbone), $2.1\text{-}2.5 \text{ ppm}$ (br, CH of the polymer backbone), $3.5\text{-}3.7 \text{ ppm}$ (br, OCH_3) ppm.

Synthesis of Poly(*tert*-butyl acrylate)-Poly(styrene) (PtBuA-PS) Diblock Copolymer from a PtBuA Macroinitiator. The synthesis of the PtBuA-PS diblock referred to as experiment SA1 in Table 6,

where a *Pt*BuA macroinitiator was used to add a styrenic block, was done similarly to the other chain extensions using the same reactor and procedure. To the flask was added 1.54 g (23.5 mmol *tert*-butyl ester) of *Pt*BuA macroinitiator ($\square = 30.4 \text{ kg}\cdot\text{mol}^{-1}$, $\square = 1.25$) followed by addition of 3.54 g (0.034 mol) styrene. The target number average degree of polymerization ($\square$) was set to 700. After appropriate nitrogen purging and heating to 115 °C, the reaction commenced. Samples were taken with a syringe periodically until the samples became too viscous to withdraw, which in this case occurred at a polymerization time of 9 minutes. The final polymer as well as the intermediate samples were precipitated in a 80 % v/v methanol/water solution and left to settle for several hours before being decanted and dried overnight in a vacuum oven at 70 °C to remove any residual solvent or non-reacted monomer. The yield was 2.24 g (44 %) and the final polymer $\square = 47.6 \text{ kg}\cdot\text{mol}^{-1}$ with $\square = 1.47$. ^1H NMR in CDCl_3 revealed the composition of *t*BuA in the copolymer to be $F_{t\text{BuA}} = 0.59$.

Synthesis of Poly(acrylic acid)-Poly(styrene) (PAA-PS) Diblock Copolymer from a PAA Macroinitiator. The procedure for experiment SA2 listed in Table 6 is for the synthesis of a segmented diblock initiated from a PAA macroinitiator that in turn was derived from a *Pt*BuA precursor. The flask was filled with the PAA macroinitiator ($\square = 25.3 \text{ kg}\cdot\text{mol}^{-1}$, $\square = 1.33$; 1.52 g, 10.39 mmol), followed by the 1,4 dioxane solvent (14.59 ml, 15.09 g) and then sealed followed by injection of styrene (5.01 g, 0.048 mol) by syringe to make a 30 wt% solution of initiator and monomer in solvent. The target $\square$ was calculated to be equal to 800. After appropriate purging with nitrogen, heating commenced. The reactor was then heated at a rate of roughly $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ and when the reactor temperature reached 70 °C, a viscous product which precipitated from the solution was formed. GPC analysis revealed insignificant change in the molecular weight of the product compared to the macroinitiator.

Synthesis of Poly(*tert*-butyl acrylate)-Poly(styrene) (*Pt*BuA-PS) Diblock Copolymer from a PS Macroinitiator. Experiment SA3 in Table 6 was done to compare whether the order in which the *t*BuA or S blocks were polymerized made any difference. Experiment SA3 used a PS macroinitiator to add a

PtBuA block as opposed to experiment SA1 that used a *PtBuA* macroinitiator to add the PS block. The same reactor and apparatus as that used for experiment SA1 was used for experiment SA3. The flask was filled with 1.54 g (0.048 mmol) of PS macroinitiator ($\square = 32.0 \text{ kg}\cdot\text{mol}^{-1}$, $\square = 1.18$), followed by the addition of 5.82 g (0.045 mol) of *tert*-butyl acrylate. The target $\square$ for the second block was ~ 950 . After appropriate sealing and nitrogen purging, the reactor was heated to 115 °C. The solution became viscous after 21 minutes of polymerization and the reactor contents were cooled and the final polymer was precipitated in a 50% v/v methanol/water mixture and left to settle for several hours, decanted and dried overnight in a vacuum oven at 70 °C to remove any residual solvent and non-reacted monomer. The final yield was 2.7 g of polymer (37 %), with $\square = 37.7 \text{ kg}\cdot\text{mol}^{-1}$, $\square = 1.62$. ^1H NMR in CDCl_3 revealed the composition of *tBuA* in the final copolymer to be $F_{t\text{BuA}} = 0.39$.

Synthesis of Poly(acrylic acid)-Poly(styrene) (PAA-PS) Diblock Copolymer from a PS Macroinitiator. Experiment SA4 in Table 6 refers to the chain extension with acrylic acid from a PS macroinitiator. The same reactor and apparatus as in the previous section was used. The flask was filled with 1.50 g (0.048 mmol) of the PS macroinitiator ($\square = 32.0 \text{ kg}\cdot\text{mol}^{-1}$, $\square = 1.18$) followed by the addition of 1,4 dioxane solvent (10.66 ml, 11.02 g to make a 30 wt% solution) and then acrylic acid (3.27 g, 0.045 mol). The target $\square$ for the acrylic acid block was calculated to be ~ 950 . After appropriate sealing and nitrogen purging, the reactor was then heated to 120 °C all while maintaining a nitrogen purge. Samples were taken periodically with a syringe and precipitated in excess hexane. After the samples became too viscous to withdraw (20 minutes), the reactor was cooled and the polymer remaining in the reactor was precipitated into excess hexane and left to settle for several hours. The solution was then decanted and dried overnight in a vacuum oven at 70 °C to remove solvent and unreacted monomer. The final yield was 3.55 g (75 %) of the acrylic acid with $\square = 41.8 \text{ kg}\cdot\text{mol}^{-1}$ and $\square = 2.57$. The molecular weight distribution was multi-modal and the composition of acrylic acid in the copolymer F_{AA} was 0.62 according to ^1H NMR in deuterated acetone.

Characterization. The overall styrene conversion for the chain extension experiments was determined by gravimetry of the dry polymer samples. The molecular weight distribution was measured using gel permeation chromatography (GPC, Waters Breeze) with tetrahydrofuran (THF) as the mobile phase. All the copolymers synthesized with an acrylic acid containing macroinitiator (experiment AA1-AA12, formulation and properties found in Table 4) were not readily soluble in THF and therefore needed to be methylated before analysis. Methylation was done by injecting (trimethylsilyl)diazomethane solution to the acrylic acid containing samples which had first been dissolved in THF with a sufficient addition of distilled water to help dissolve the polymer. The copolymers initiated by *tert*-butyl acrylate containing macroinitiators (experiments TA1-TA8, see Tables 1 and 2) were soluble in organic solvents and therefore did not need further treatment prior to GPC analysis. The flow rate of the GPC mobile phase was set to 0.3 mL·min⁻¹. The GPC was equipped with 3 Waters Styragel® HR columns (HR1 with molecular weight measurement range of 10² – 5 x 10³ g·mol⁻¹, HR2 with molecular weight measurement range of 5 x 10² – 2 x 10⁴ g·mol⁻¹ and HR4 with molecular weight measurement range 5 x 10³ – 6 x 10⁵ g·mol⁻¹) and a guard column were used. The columns were heated to 40 °C during the analysis. The molecular weights were determined by calibration in THF with narrow molecular weight distribution poly(styrene) standards. To analyze the samples passing through the GPC, both ultra-violet (Model UV 2487) and differential refractive index (Model RI 2410) detectors were used. The UV detector was set to a wavelength of 255 nm to detect the aromatic rings in the poly(styrene) containing copolymers. ¹H nuclear magnetic resonance (NMR) was performed on the copolymers to identify the ratio of the acrylate (*tert*-butyl acrylate or acrylic acid) with respect to the styrene and to estimate the fraction of styrene added after chain extension from the initiators. After methylation, the copolymer samples taken during experiments AA1-AA12 (Table 4) were soluble in chloroform and were analyzed in the same manner as the copolymers from experiments TA1-TA8. The ¹H NMR measurements were done with a 400 MHz Varian Gemini 2000 spectrometer using deuterated chloroform (CDCl₃, Cambridge Isotope Laboratories Inc.) as the solvent in 5 mm Up NMR tubes. After injecting and shimming, the samples were scanned 16 times. The copolymer compositions were estimated by

comparing the resonances due to the aromatic protons corresponding to the styrene monomers at $\delta = 6.8\text{--}7.1$ ppm and the resonances corresponding to the aliphatic backbone and the *tert*-butyl groups from $\delta = 1.5\text{--}2.5$ ppm (copolymers from experiment TA1-TA8) or the resonances corresponding to the aliphatic backbone and the acrylic acid groups from $\delta = 1.5\text{--}2.5$ ppm (copolymers from experiment AA1-AA12).

Results and Discussion

Chain Extension of Poly(*tert*-butyl acrylate-*ran*-styrene) (P(*t*BuA-*r*-S)) Macroinitiators with Styrene. To determine the ability of protected acrylic acid containing polymers to initiate a second batch of monomer by nitroxide-mediated polymerization, several P(*t*BuA-*r*-S) random copolymers synthesized previously using two levels of additional SG1 free nitroxide to BlocBuilder® initiator ($r = [\text{SG1}]_0/[\text{BlocBuilder}^\text{®}]_0 = 0\text{--}0.045$ where $[\text{SG1}]_0$ is the initial concentration of free nitroxide added and $[\text{BlocBuilder}^\text{®}]_0$ is the initial concentration of BlocBuilder® added)²⁸ were used as macroinitiators for bulk polymerization at 115 °C. The P(*t*BuA-*r*-S) macroinitiators were of various compositions ranging from 35 to 73 mol% *t*BuA in the copolymer (Table 2). The use of a PtBuA homopolymer as a macroinitiator for styrene polymerization will be detailed in a later section. Entries TA1-TA4 in Table 2 refer to macroinitiators made without any additional SG1 free nitroxide while entries TA5-TA8 were made with $r = 0.045$. The changes in molecular weight after styrene initiation from macroinitiators TA1-TA8 are summarized in Table 3 while GPC chromatograms indicate the molecular weight distributions after various chain extension times derived from P(*t*BuA-*r*-S) macroinitiators made with no free nitroxide (Figure 1) and with $r = 0.045$ (Figure 2). Compositions of the block copolymers after chain extension in addition to molecular weight distribution data are listed in Table 2. For macroinitiators made without any additional free nitroxide, chain extension with styrene in bulk at 115 °C revealed that remained low and only marginally increased with a maximum of = 1.39 during the course of the polymerization (Table 2). The macroinitiator 's were all originally in the range from 1.21-1.27 and varied from 1.25-1.39 after completion of chain extension as indicated

in Table 3 (when samples were too viscous to remove by syringe). Further, the molecular weight distributions remained narrow and monomodal as indicated by the GPC chromatograms summarized in Figure 1. The P(*t*BuA-*r*-S)-PS block copolymer $\overline{M}_w$ increased linearly with styrene conversion over the range studied as illustrated in the insets to the chromatograms shown in Figure 1 and Figure 3 in more detail. The linear increase in $\overline{M}_w$ with conversion combined with the retention of a narrow, monomodal molecular weight distribution suggested that a high proportion of the chains were capped with SG1 and sufficient “living” behavior was attained. Also, no apparent influence of the P(*t*BuA-*r*-S) macroinitiator composition was observed on the evolution of the molecular weight distribution during chain extension.

For P(*t*BuA-*r*-S) macroinitiators made originally with $r = 0.045$ (entries TA5-TA8 in Tables 1 and 2), chain extension with styrene also indicated a linear relationship between block copolymer $\overline{M}_w$ and styrene conversion over the range studied as indicated by the insets to Figure 2 and in more detail in Figure 3. The macroinitiator $\overline{M}_w$ before styrene addition ranged from 1.13-1.57 for the various macroinitiators. The diblock products became richer in styrene as expected after chain extension (Table 2) while the resulting P(*t*BuA-*r*-S)-PS block copolymers had $\overline{M}_w$ ranging from 1.24-1.35 after chain extension and all exhibited relatively narrow, monomodal molecular weight distributions as shown in Figure 2. The use of additional SG1 free nitroxide to synthesize the P(*t*BuA-*r*-S) macroinitiators (TA5-TA8) also did not strongly affect the “livingness” of the chain extension polymerizations. Additionally, the composition of the macroinitiators did not have a dramatic effect on the ability to initiate the second block of styrene. With or without free nitroxide, the diblock products only exhibited a mild increase in $\overline{M}_w$ and remained relatively low compared to the macroinitiator $\overline{M}_w$. These findings suggest well-defined P(*t*BuA-*r*-S)-PS block copolymer precursors for P(AA-*r*-S)-PS can be effectively made from a variety of P(*t*BuA-*r*-S) macroinitiators at the given conditions.

The conversion and $\overline{M}_w$ were determined at several polymerization times for each of the chain extensions from P(*t*BuA-*r*-S) macroinitiators and are plotted in Figure 3. Generally, the styrene conversions varied from a little less than 10% after 10 minutes of polymerization to a little less than

30% after 30-40 minutes after chain extension was initiated. We estimated the apparent slope $k_p[P^*]$ from the semi-logarithmic kinetic plots of $\ln[1/(1-X)]$ versus time t where k_p is the propagation rate constant, $[P^*]$ is the concentration of propagating macro-radicals and X is the monomer conversion. The values of $k_p[P^*]$ at 115 °C varied over a relatively wide range from about $1-7 \times 10^{-4} \text{ s}^{-1}$ for the styrene chain extensions from the various P(*t*BuA-*r*-S) macroinitiators as differences in macroinitiator chain length and conversions might have affected the number of propagating chains and the resulting kinetics. However, the $k_p[P^*]$ values from the styrene chain extension are still not very different from the $k_p[P^*]$ reported by us earlier for *t*BuA/styrene random copolymerizations which ranged from $0.8-3.2 \times 10^{-4} \text{ s}^{-1}$.²⁸ We are now planning to examine in more detail the effect of P*t*BuA macroinitiator chain length at a given conversion to determine more accurately how $k_p[P^*]$ varies with these parameters for chain extensions with styrene and other monomers.

Chain Extension of Poly(acrylic acid-*ran*-styrene) (P(AA-*r*-S)) Macroinitiators with Styrene. A second series of experiments was performed to observe the ability of P(AA-*r*-S) copolymers to initiate a second block of styrene. These particular macroinitiators were initially synthesized using acrylic acid directly without it being in the protected *tert*-butyl acrylate form and should indicate how the effect of protection affected “livingness” of the chains. The P(AA-*r*-S) macroinitiators were prepared previously with variable acrylic acid concentration and different levels of added free nitroxide ($r = 0, 0.045$ and 0.09). The molecular characterization of the P(AA-*r*-S) macroinitiators is summarized in Table 4. Table 4 also summarizes the molecular characteristics of the P(AA-*r*-S)-PS products after chain extension with styrene of the P(AA-*r*-S) macroinitiators in 1,4 dioxane solution at 120 °C. The macroinitiators previously synthesized with no additional SG1 free nitroxide were identified as AA1-AA4 in Table 4. Other sets of experiments using macroinitiators originally synthesized with $r = 0.045$ and 0.09 were identified as AA5-AA8 and AA9-AA12, respectively, in Table 4. Table 5 summarizes the molecular weight data from GPC for all the experiments using P(AA-*r*-S) macroinitiators at various times of the chain extension. Figures 4-6 show GPC chromatograms of the products at various times of chain extension from macroinitiators made originally with $r = 0, 0.045$ and 0.09 , respectively.

Figure 4 shows the evolution of the molecular weight distribution of P(AA-*r*-S)-PS copolymers initiated by the various P(AA-*r*-S) macroinitiators originally synthesized without any additional SG1 free nitroxide (entries AA1-AA4 in Table 4). The molecular weight distribution broadened considerably, particularly when the macroinitiator had a higher concentration of acrylic acid groups. The $\overline{M}_w$ increased to ~ 1.7 after 50 minutes of styrene polymerization that was initiated with a P(AA-*r*-S) macroinitiator ($\overline{M}_n = 23.6 \text{ kg}\cdot\text{mol}^{-1}$, $\overline{M}_w = 1.42$, $F_{AA} = 0.42$ (entry AA1 in Table 4). For styrene polymerization that was initiated by a P(AA-*r*-S) with $F_{AA} = 0.72$ (entry AA4 in Table 4; $\overline{M}_n = 21.1 \text{ kg}\cdot\text{mol}^{-1}$ and $\overline{M}_w = 1.48$), the $\overline{M}_w$ increased to 2.11 after 50 minutes of polymerization. Further, in all cases, the $\overline{M}_w$ increased quite rapidly at the onset of the chain extension (see Table 5) and the $\overline{M}_n$ essentially reached a plateau and the $\overline{M}_w$ remained above 1.5 during the entire course of the chain extension. These results are consistent with a greater number of dead chains caused by degradative side reactions of the SG1 groups with the acrylic acid monomer⁴⁰. This would result in more termination reactions and more dead chains, particularly when the acrylic acid content was high in the macroinitiator. It is not certain whether the degradative side reactions proceeds with chain ends or with nitroxides. Perhaps tagging the BlocBuilder® initiator with a fluorescent group will enable the tracking of the degradation process. In some cases in Figure 4, a secondary peak corresponding to dead macroinitiator chains could be observed. Thus, in contrast to the P(*t*BuA-*r*-S) macroinitiators, the composition of the P(AA-*r*-S) macroinitiator, made originally without any free nitroxide, affected the ability to cleanly initiate a second block of styrene.

When additional SG1 free nitroxide at $r = 0.045$ was added to synthesize the P(AA-*r*-S) macroinitiator, the same general trend was observed as for the case without any additional free nitroxide. The molecular weight distribution broadened more when initiating chain extension with macroinitiators having higher acrylic acid content. For example, the P(AA-*r*-S) macroinitiator with the lowest acrylic acid concentration (entry AA5 in Table 4, $F_{AA} = 0.50$, $\overline{M}_n = 20.0 \text{ kg}\cdot\text{mol}^{-1}$ and $\overline{M}_w = 1.35$) was able to initiate styrene polymerization as indicated by the steady increase in $\overline{M}_n$ up to 30.8

kg·mol⁻¹ and a relatively mild increase in $\bar{M}_w$ up to 1.50 after 60 minutes (Table 5). However, the macroinitiator with the highest acrylic acid concentration (entry AA7 in Table 4, $F_{AA} = 0.83$, $\bar{M}_w = 24.3$ kg·mol⁻¹ and $\bar{M}_n = 1.34$) was able to initiate some styrene polymerization with $\bar{M}_w$ increasing up to 28.5 kg·mol⁻¹ but $\bar{M}_n$ rose to 2.15 after 58 minutes (Table 5). At longer times, little change in $\bar{M}_w$ was observed and $\bar{M}_n$ continued to rise. As observed by the GPC traces in Figure 5, some of the chains were extended but in many cases such as Figure 5d) (derived from the macroinitiator with the highest acrylic acid content), the peak corresponding to the macroinitiator could be clearly seen as a separate peak compared to the peak corresponding to the growing chains. These observations suggest a significant concentration of dead chains were present, particularly when the macroinitiator had a high acrylic acid content. These results suggest that adding more free nitroxide at a level of $r = 0.045$ to produce the P(AA-*r*-S) macroinitiator was not sufficient to yield a high degree of “livingness”, particularly when the macroinitiator was rich in acrylic acid.

When the P(AA-*r*-S) macroinitiators were synthesized originally with the highest level of free nitroxide ($r = 0.09$), the subsequent chain extension with styrene (entries AA9-AA12 in Table 4) resulted in broader molecular weight distributions as shown in Figure 6 but not to the degree observed with P(AA-*r*-S) macroinitiators made with lower r values. The highest $\bar{M}_w$ of the P(AA-*r*-S)-PS product was 1.74 which occurred when using the P(AA-*r*-S) macroinitiator with the highest acrylic acid concentration (entry AA12 in Table 4; $F_{AA} = 0.78$, $\bar{M}_w = 27.4$ kg·mol⁻¹, $\bar{M}_n = 1.43$). These observations suggest that additional free nitroxide compensated for the nitroxide lost to degradative side reactions with the acrylic acid. However, even at the highest level of free nitroxide added, the molecular weight distributions of the P(AA-*r*-S)-PS block copolymers still broadened and were higher than those of the P(*t*BuA-*r*-S)-PS block copolymers containing the protected form of acrylic acid. To achieve comparable “livingness” to *tert*-butyl acrylate containing polymers with nitroxide-mediated polymerization, acrylic acid containing polymers needed a higher concentration of free nitroxide to compensate for the degradative side reactions. In this particular case of acrylic acid polymerizations

with nitroxides, it may not be easier to directly polymerize acrylic acid compared to the protected monomer, which is in contrast to one of the advantages typically offered by controlled radical polymerizations. These observations thus have important ramifications when synthesizing block copolymers by nitroxide-mediated polymerization where acrylic acid functionality is desired.

Synthesis of Poly(acrylic acid)-Poly(styrene) (PAA-PS) Diblock Copolymers. Mindful of our previous observations concerning acrylic acid/styrene nitroxide-mediated copolymerization and subsequent chain extension, we explored different permutations to derive PAA-PS diblocks cleanly with a monomodal and narrow molecular weight distribution. There are several ways to obtain a PAA-PS diblock by nitroxide-mediated polymerization as summarized in Scheme 2. The first route was to use an SG1-capped *Pt*BuA homopolymer as a macroinitiator for a second styrenic block to yield the resulting *Pt*BuA-PS diblock that could then be treated with trifluoroacetic acid (TFA) to de-protect the acrylic acid yielding a PAA-PS polymer (entry SA1 in Table 6). The second method used the same *Pt*BuA macroinitiator as SA1 but it was first treated with TFA to produce a PAA macroinitiator for the polymerization of styrene (entry SA2 in Table 6). A comparison of these two experiments would reveal the effect of TFA treatment of the *Pt*BuA on the initiation of a styrene segment. Experiments SA1 and SA3 in Table 6 were done to compare the effect of switching the order of polymerization on the “livingness”. Experiment SA3 in Table 6 instead used SG1-capped PS to initiate *t*BuA polymerization followed by deprotection of the *tert*-butyl groups in the PS-*Pt*BuA to give the PS-PAA diblock. Finally, experiment SA4 in Table 6 used the same SG1-capped PS macroinitiator to initiate the direct polymerization of acrylic acid to give the PS-PAA diblock. Additionally, another route, which has been indicated previously, is to use a PAA macroinitiator made from the direct polymerization of acrylic acid to initiate a second batch styrene. Specifically the chain extension was done using an acrylic acid/styrene mixture as the second block²³. The chain extension was deemed to be in good control as exemplified by monomodal molecular weight distributions and $\text{M}_w/\text{M}_n = 1.3\text{-}1.4$ provided that the PAA macroinitiator had a relatively low molecular weight ($\text{M}_n = 7.1 \text{ kg}\cdot\text{mol}^{-1}$).²³

Experiment SA1 used a PtBuA ($M_n = 30.4$ kg/mol, $M_w/M_n = 1.25$) synthesized in bulk at 115 °C with $r = 0.045$ as a macroinitiator for the polymerization of a second batch of styrene. The resulting PtBuA-PS diblock retained a monomodal narrow molecular weight distribution ($M_n = 47.7$ kg/mol, $M_w/M_n = 1.47$) that was subsequently retained after removal of the *tert*-butyl group. The GPC chromatograms in Figure 7a) show the shift in molecular weight from the PtBuA precursor to the PtBuA-PS diblock along with the retention of a relatively narrow molecular weight distribution. These observations agree relatively well with those of the styrene chain extensions with the P(*t*BuA-*r*-S) random copolymers as macroinitiators. Experiment SA2 took the same PtBuA macroinitiator as experiment SA1 except the *tert*-butyl protecting groups were converted to acrylic acid groups prior to styrene polymerization. The resulting PAA retained a narrow molecular weight distribution ($M_n = 25.3$ kg/mol and $M_w/M_n = 1.33$ by GPC after suitable methylation of the acrylic acid groups). While heating the contents comprising the SA2 polymerization (PAA, styrene monomer and 1,4 dioxane solvent), some precipitation occurred when the mixture reached approximately 70 °C. The heating was then stopped. The product was barely soluble in THF and some of it never went into solution. As seen in Figure 7b), the GPC chromatogram of the product that was still soluble in THF revealed negligible change in molecular weight distribution and the average molecular weight, suggesting that the TFA treatment degraded the SG1 chain end groups and inhibited further polymerization from the PAA chains.

These results underscore the key issues of SG1-mediated polymerization of acrylic acid. The effect of PAA as a macroinitiator for nitroxide-mediated styrene polymerization in solution^{23,26} and miniemulsion conditions^{48,49} has also been studied under milder conditions. In 1,4 dioxane solution, Lefay et al. used a low molecular weight PAA macroinitiator ($M_n = 1.8$ kg·mol⁻¹) that was synthesized at 41% conversion to ensure high concentration of active SG1 groups for subsequent chain extensions with styrene and *n*-butyl acrylate²⁶. Some residual PAA was detected that did not initiate the second block but chain extension with styrene still resulted in retention of a narrow molecular weight

distribution. In miniemulsion, the acrylic acid groups were neutralized with base prior to polymerization to not only enhance the water solubility of the macroinitiator but also to minimize the effect of acrylic acid degradation of the SG1 nitroxide^{48,49}. Delaittre et al. found the miniemulsion polymerization initiated by the neutralized PAA ($\bar{M}_n = 1.9 \text{ kg} \cdot \text{mol}^{-1}$, $\bar{M}_w/\bar{M}_n = 1.17$) cleanly proceeded for styrene polymerization with stable latexes being formed and $\bar{M}_w/\bar{M}_n$ remaining below 1.5 up to styrene conversions of 80%⁴⁹. Our experiment emphasized the importance of maintaining the SG1 end group fidelity as we found styrene polymerization was effectively inhibited due to strong acid degradation of the SG1 prior to chain extension.

The experiment listed as SA3 in Table 6 attempted to determine whether it mattered if the styrene block or the *tert*-butyl acrylate block was polymerized first. The PS macroinitiator ($\bar{M}_n = 32.0 \text{ kg} \cdot \text{mol}^{-1}$, $\bar{M}_w/\bar{M}_n = 1.18$) was able to initiate the polymerization of the second block of *tert*-butyl acrylate cleanly with a moderate increase in the polydispersity ($\bar{M}_w/\bar{M}_n = 1.62$). The broadness of the molecular weight distribution as noticed in Figure 7c) suggests that despite the narrow molecular weight distribution of the macroinitiator, some chains were “dead”. Thus, there seems to be more broadening of the molecular weight distribution when using a PS macroinitiator instead of a *PtBuA* macroinitiator. Perhaps the propensity of styrene to thermally polymerize in nitroxide-mediated polymerization and conventional radical polymerization⁵⁰⁻⁵², particularly at the temperatures of 115-120 °C used to make the PS macroinitiator initially, caused a higher concentration of dead PS chains to be formed which could not re-initiate *tBuA* polymerization.

The experiment SA4 listed in Table 6 used the same PS precursor as experiment SA3 except that the second block added to it was the unprotected acrylic acid instead of the *tert*-butyl acrylate as the protected form of acrylic acid. In this case, the PS-PAA diblock increased in molecular weight compared to the PS macroinitiator but its molecular weight distribution was considerably broader compared to the PS macroinitiator ($\bar{M}_n = 41.8 \text{ kg/mol}$ and $\bar{M}_w/\bar{M}_n = 2.58$) as illustrated by the GPC chromatogram shown in Figure 7d). It shows that the acrylic acid being added as the second block

could have been degrading the SG1 end groups on the PS macroinitiators, resulting in less control of the polymerization which was obvious from the multi-modal chromatogram shown in Figure 6d). Laruelle et al used a low molecular weight SG1-capped PS ($M_n = 1.7 \text{ kg}\cdot\text{mol}^{-1}$, $M_w = 1.25$) as a macroinitiator for direct AA polymerization⁵³. The PS macroinitiator was originally polymerized using SG1 free nitroxide and *N-tert-butyl-N-(1-diethylphosphono-(2,2-dimethylpropyl))-O-1-methoxycarbonyl-ethylhydroxylamine* (MONAMS) initiator with $r = 0.05$ at 120 °C in bulk. Conversion was kept low (about 17% based on the theoretical target molecular weight) by stopping the polymerization after 20 minutes to ensure a high degree of SG1 end-group fidelity. In contrast, the PS macroinitiator used here was much higher in molecular weight ($M_n = 32.0 \text{ kg}\cdot\text{mol}^{-1}$) and likely contained more “dead” chains since it was polymerized to higher conversions where termination reactions become more likely. Also, the higher molecular weight PS macroinitiator was likely more susceptible to SG1 end group degradation by the AA monomer since the concentration of SG1 end groups was much lower than that used by Laruelle et al.⁵³ Furthermore, the study by Laruelle added more free nitroxide (9 mol% relative to the macroinitiator) during the chain extension with acrylic acid which could have prevented some attack of the monomer on the SG1-terminated chain ends of the PS macroinitiator.⁵³ These factors highlight the caution needed when making higher molecular weight PS-PAA block copolymers by nitroxide-mediated polymerization. Since the PS macroinitiator was much higher in molecular weight, was polymerized to higher conversion and we did not introduce more free nitroxide when adding the AA for the second block, the probability of chain end degradation was likely higher and the resulting block copolymer possessed a broad molecular weight distribution.

These sets of experiments provide evidence that PAA-PS diblocks synthesized by nitroxide-mediated polymerization may be more easily produced when the acrylic acid is in the protected form of *tert*-butyl acrylate, and only after adding all desired blocks is it suggested to remove the *tert*-butyl protecting groups. The results presented here also indicate the importance of the macroinitiator chain length for subsequent chain extension. In contrast to previous studies that employed much shorter molecular weight PAA or PS macroinitiators with $M_n \sim 2 \text{ kg}\cdot\text{mol}^{-1}$, the higher molecular weight

macroinitiators studied here made them more susceptible to the effect of side reactions. Strict control of the conditions such as conversion should be employed when making the macroinitiators in order to concretely compare “livingness” as a function of chain length. We are currently examining in more detail the effect of *Pt*BuA and PAA macroinitiator chain length on the styrene chain extension kinetics and molecular weight distribution with the aim of developing block copolymers with highly controlled microstructure and high target molecular weights.

Conclusion

This study examined the ability of SG1-capped poly(*tert*-butyl acrylate-*r*-styrene) (P(*t*BuA-*r*-S)) and poly(acrylic acid-*r*-styrene) (P(AA-*r*-S)) macroinitiators of various compositions to extend the chains with poly(styrene) segments without adding more free nitroxide initiator. The results of chain extension experiments TA1-TA8 (Tables 2-3) and AA1-AA12 (Tables 4-5) showed that the protected acrylate (with *t*BuA as a monomer, experiments TA1-TA8) yielded consistently narrower molecular weight distributions while maintaining monomodality. The results from experiments AA1-AA12, which had the acrylic acid segments in the unprotected form, showed that even though the macroinitiator was capable of re-initiating the polymerization of a second styrene block, the final chain-extended polymers possessed broader molecular weight distributions compared to the initial macroinitiator and much broader molecular weight distributions compared to their counterparts synthesized with acrylic acid in its protected *t*BuA form (TA1-TA8). For the acrylic acid polymerizations, only at the highest level of additional SG1 free nitroxide used ($r = 0.09$) did the polydispersity of the products start approaching that observed for chain extensions using the *tert*-butyl acrylate made with no additional free SG1 nitroxide or $r = 0.045$. Additional experiments to produce PAA-PS segmented diblocks indicated that the best technique to produce such block copolymers with nitroxide-mediated polymerization is likely to use the protected form of acrylic acid such as *tert*-butyl acrylate to make the macroinitiator and then remove the *tert*-butyl protecting group after the second styrene block was added.

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FIGURE CAPTIONS

Figure 1: Gel permeation chromatograms (GPC) for styrene chain extension in bulk at 115 °C using various poly(*tert*-butylacrylate-*ran*-styrene) random copolymer macroinitiators that were originally synthesized without any additional SG1 free nitroxide for: a) samples taken at various times during experiment TA1; b) samples taken at various times during experiment TA2; c) samples taken at various times during experiment TA3; d) samples taken at various times during experiment TA4. The inset to each figure indicates the number average molecular weight  versus conversion plots for the respective polymerization. All formulations and characterization of experiments TA1-TA4 is listed in Tables 1, 2 and 3.

Figure 2: Gel permeation chromatograms (GPC) for styrene chain extension in bulk at 115 °C using various poly(*tert*-butyl acrylate-*ran*-styrene) random copolymer macroinitiators that were originally synthesized with $r = [\text{SG1}]_0/[\text{BlocBuilder}^{\text{®}}]_0 = 0.045$ for: a) samples taken at various times during experiment TA5; b) samples taken at various times during experiment TA6; c) samples taken at various times during experiment TA7; d) samples taken at various times during experiment TA8. The inset to each figure indicates the number average molecular weight  versus conversion plots for the respective polymerization. All formulations and characterization of experiments TA5-TA8 are listed in Tables 1, 2 and 3.

Figure 3: Number average molecular weight  versus conversion for styrene chain extensions at 115 °C from poly(*tert*-butyl acrylate-*ran*-styrene) macroinitiators that were originally synthesized a) without additional SG1 free nitroxide and b) a molar ratio of initially added SG1 free nitroxide relative to initially added BlocBuilder initiator of $r = 0.045$. In a) the symbols correspond to experiment TA1 (filled squares, ) , TA2 (filled diamonds, ) , TA3 (filled triangles, ) and TA4 (filled circles, ) . In b), the symbols correspond to experiment TA5 (open squares, ) , TA6 (open diamonds, ) , TA7 (open

triangles, Δ) and TA8 (open circles, $\circ$). All formulations for experiments TA1-TA8 are summarized in Table 1 while all characterization of experiments TA1-TA8 are summarized in Table 2.

Figure 4: Gel permeation chromatograms (GPC) for styrene chain extension in bulk at 120 °C using various poly(acrylic acid-*ran*-styrene) random copolymer macroinitiators (P(AA-*r*-S)) that were originally synthesized without any additional SG1 free nitroxide for: a) samples taken at various times during experiment AA1; b) samples taken at various times during experiment AA2; c) samples taken at various times during experiment AA3; d) samples taken at various times during experiment AA4. All characterization of experiments AA1-AA4 is listed in Tables 4 and 5.

Figure 5: Gel permeation chromatograms (GPC) for styrene chain extension in bulk at 120 °C using various poly(acrylic acid-*ran*-styrene) random copolymer macroinitiators (P(AA-*r*-S)) that were originally synthesized with $r = [\text{SG1}]_0/[\text{BlocBuilder}^{\text{®}}]_0 = 0.045$ for: a) samples taken at various times during experiment AA5; b) samples taken at various times during experiment AA6; c) samples taken at various times during experiment AA7; d) samples taken at various times during experiment AA8. All characterization of experiments AA5-AA8 is listed in Tables 4 and 5.

Figure 6: Gel permeation chromatograms (GPC) for styrene chain extension in bulk at 120 °C using various poly(acrylic acid-*ran*-styrene) (P(AA-*r*-S)) random copolymer macroinitiators that were originally synthesized with $r = [\text{SG1}]_0/[\text{BlocBuilder}^{\text{®}}]_0 = 0.09$ for: a) samples taken at various times during experiment AA9; b) samples taken at various times during experiment AA10; c) samples taken at various times during experiment AA11; d) samples taken at various times during experiment AA12. All characterization of experiments AA9-AA12 is listed in Tables 4 and 5.

Figure 7: Gel permeation chromatograms (GPC) during chain extensions from various poly(*tert*-butyl acrylate) (PtBuA), poly(acrylic acid) (PAA) or poly(styrene) (PS) macroinitiators: a) PtBuA macroinitiator (entry SA1 in Table 6) (grey line) ($M_n = 30.4 \text{ kg}\cdot\text{mol}^{-1}$, $M_w/M_n = 1.25$) before and after chain extension (black line) ($M_n = 47.7 \text{ kg}\cdot\text{mol}^{-1}$, $M_w/M_n = 1.48$, polymerization time = 9 min) with

styrene at 115 °C in bulk; b) PtBuA macroinitiator converted to PAA (entry SA2 in Table 6) (grey line) ($\square = 25.3 \text{ kg}\cdot\text{mol}^{-1}$, $\square = 1.33$) before and after chain extension (black line) with styrene at 120 °C in 50 wt% 1,4 dioxane solution; c) PS macroinitiator (entry SA3 in Table 6) ($\square = 32.0 \text{ kg}\cdot\text{mol}^{-1}$, $\square = 1.18$) before (grey line) and after chain extension with *tert*-butyl acrylate (black line) ($\square = 37.7 \text{ kg}\cdot\text{mol}^{-1}$, $\square = 1.62$, polymerization time = 21 min) at 115 °C in bulk; d) PS macroinitiator (entry SA4 in Table 6) ($\square = 32.0 \text{ kg}\cdot\text{mol}^{-1}$, $\square = 1.18$) before (grey line) and after chain extension with acrylic acid (black line) ($\square = 41.8 \text{ kg}\cdot\text{mol}^{-1}$, $\square = 2.58$, polymerization time = 21 min) at 120 °C in 50 wt% 1,4 dioxane solution.

Scheme 1. Structures and acronyms of various alkoxyamine mediators and unimolecular initiators derived from the SG1 family: a) *N-tert*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide (SG1); b) *N-tert*-butyl-*N*-1-diethylphosphono-2,2-dimethylpropyl-O-1-methoxycarbonyl ethyl hydroxylamine (MONAMS) and c) 2-[*N-tert*-butyl-2,2-dimethylpropyl]aminoxy] propionic acid (BlocBuilder®).

Scheme 2. Routes to produce poly(acrylic acid)-poly(styrene) (PAA-PS) diblock copolymers by nitroxide-mediated polymerization of poly(*tert*-butyl acrylate) (PtBuA) or PS macroinitiators. The various routes termed SA1, SA2, SA3 and SA4 refer to the experiments listed in Table 6.

Table 1: Formulations of Chain Extensions with Styrene Initiated by Poly(*tert*-butyl acrylate-*ran*-styrene) (P(*t*BuA-*r*-S)) and Poly(acrylic acid-*ran*-styrene) (P(AA-*r*-S)) Random Copolymers

Experiment ID ^a	Macroinitiator Characteristics				m_{styrene} (g)	m_{solvent} (g) ^c	T (°C)
	mass (g)	$[\eta]$ (kg·mol ⁻¹) ^b	M_n (g/mol) ^b	X			
TA1	1.00	23.8	1.18	0.35	9.04	bulk	115
TA2	1.00	20.3	1.19	0.61	7.90	bulk	115
TA3	1.00	17.9	1.27	0.24	3.01	bulk	115
TA4	1.00	13.4	1.22	0.38	3.90	bulk	115
TA5	1.50	18.6	1.13	0.45	4.23	bulk	115
TA6	1.50	19.6	1.15	0.42	3.96	bulk	115
TA7	1.50	22.2	1.14	0.38	3.51	bulk	115
TA8	1.50	25.8	1.57	0.42	3.20	bulk	115
AA1	1.00	23.6	1.42	0.77	2.35	3.28	120
AA2	1.00	19.7	1.40	0.56	2.81	3.78	120
AA3	1.00	21.6	1.37	0.55	2.40	3.56	120
AA4	1.00	21.1	1.48	0.69	2.45	3.63	120
AA5	1.03	20.0	1.35	0.46	2.90	3.58	120
AA6	1.00	25.1	1.34	0.85	2.07	3.06	120
AA7	1.00	24.3	1.34	0.75	2.18	6.97 ^d	120
AA8	1.00	24.1	1.46	0.65	2.20	7.40 ^d	120
AA9	1.04	23.7	1.23	0.43	2.29	7.76 ^d	120
AA10	1.02	26.7	1.47	0.47	1.96	6.95 ^d	120
AA11	1.01	28.8	1.34	0.43	1.83	7.06 ^d	120
AA12	1.03	27.4	1.43	0.56	1.97	6.87 ^d	120

^aExperiment ID refers to chain extensions from poly(*tert*-butyl acrylate-*ran*-styrene) macroinitiators denoted by TA and from poly(acrylic acid-*ran*-styrene) macroinitiators denoted by AA.

^bNumber average molecular weight ($\bar{M}_n$), weight average molecular weight ($\bar{M}_w$) and polydispersity index ($\bar{M}_w/\bar{M}_n$) determined by gel permeation chromatography (GPC) relative to linear poly(styrene) standards in tetrahydrofuran (THF) at 40 °C.

^cThe solvent used for the chain extensions with styrene from poly(acrylic acid-*ran*-styrene) macroinitiators was 1,4 dioxane.

^dThe chain extension experiments noted used a 30 wt% loading of macroinitiator and styrene monomer compared to the other chain extension experiments from poly(acrylic acid-*ran*-styrene) macroinitiators which used a 50 wt% loading of macroinitiator and styrene monomer.

(Table 1 continued above)

Table 2. Characterization of Poly(*tert*-butyl acrylate-*ran*-styrene) (P(*t*BuA-*r*-S)) Macroinitiators and Resulting Block Copolymers after Chain Extension with Styrene (P(*t*BuA-*r*-S)-PS)) at 115 °C in Bulk.

Experiment ID	r^a	$F_{tBuA, initiator}^b$	$\bar{M}_n^c$ (kg·mol ⁻¹)	Initiator $\bar{M}_n^c$	$\bar{M}_w^c$ (kg·mol ⁻¹)	Block Copolymer $\bar{M}_n^c$	$F_{tBuA, block copolymer}^b$
TA1	0	0.35	23.8	1.18	66.3	1.39	0.26
TA2	0	0.42	20.3	1.19	57.1	1.39	0.27
TA3	0	0.48	17.9	1.27	44.6	1.25	0.30
TA4	0	0.66	13.4	1.22	37.7	1.34	0.41
TA5	0.045	0.29	18.6	1.13	34.6	1.24	0.23
TA6	0.045	0.36	19.6	1.15	35.6	1.24	0.29
TA7	0.045	0.50	22.2	1.14	43.7	1.27	0.34
TA8	0.045	0.73	25.8	1.57	46.5	1.35	0.54

^a r = initial molar concentration of SG1 free nitroxide addition relative to initial molar concentration BlocBuilder® initiator = $[SG1]_0/[BlocBuilder]_0$

^b F_{tBuA} is the molar fraction of *tert*-butyl acrylate in the final polymer determined by ¹H nuclear magnetic resonance (NMR).

^cNumber average molecular weight ($\bar{M}_n$), weight average molecular weight ($\bar{M}_w$) and polydispersity index ($\bar{M}_w/\bar{M}_n$) determined by gel permeation chromatography (GPC) relative to linear poly(styrene) standards in tetrahydrofuran (THF) at 40 °C.

Table 3. Molecular Weight Characterization of Poly(*tert*-butyl acrylate-*ran*-styrene)-Poly(styrene) (P(*t*BuA-*r*-S)-PS)) Block Copolymers at Various Polymerization Times Initiated by Poly(*tert*-butyl acrylate-*ran*-styrene) Copolymers at 115 °C in Bulk.

Experiment ID ^a	time (min)	$\bar{M}_n$ (kg·mol ⁻¹)	$\bar{M}_w/\bar{M}_n$	Experiment ID ^a	time (min)	$\bar{M}_n$ (kg·mol ⁻¹)	$\bar{M}_w/\bar{M}_n$
TA1	0	34.5	1.22	TA5	0	27.5	1.15
	2	39.7	1.26		5	29.2	1.22
	5	40.1	1.49		10	34.6	1.24
	10	52.4	1.32	TA6	0	25.4	1.20
	20	58.8	1.35		2	28	1.21
	41	66.3	1.39		6	34.8	1.17
TA2	1	33.7	1.30		11	35.6	1.24
	6	38.4	1.27	TA7	0	31.8	1.20
	14	48.8	1.29		2	35.9	1.17
	23	52.7	1.32		5	39.3	1.24
	30	57.9	1.31		10	39.3	1.27
	35	57.1	1.39	TA8	0	22.5	1.85
TA3	0	25.0	1.19		2	24.2	2.02
	5	32.5	1.22				
	10	36.3	1.25				
	20	40.5	1.27				
	30	44.6	1.25				
TA4	0	27.6	1.31				
	4	32.8	1.29				

9	36.1	1.28	5	32.1	1.28
13	36.9	1.32	8	35.7	1.38
18	37.7	1.34	12	46.5	1.35

^aExperiment ID refers to the experiments listed in Tables 1 and 2.

^bNumber average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (PDI) determined by gel permeation chromatography (GPC) relative to linear poly(styrene) standards in tetrahydrofuran (THF) at 40 °C.

(Table 3 continued above)

Table 4. Characterization of Poly(acrylic acid-*ran*-styrene) (P(AA-*r*-S)) Macroinitiators and Resulting Block Copolymers after Chain Extension with Styrene (P(AA-*r*-S)-PS)) at 120 °C in 50 wt% 1,4 Dioxane Solution.

Experiment ID	r^a	$F_{AA, \text{initiator}}^b$	$\square^c$ ($\text{kg} \cdot \text{mol}^{-1}$)	Initiator $\square^c$	$\square^c$ ($\text{kg} \cdot \text{mol}^{-1}$)	Block Copolymer $\square^c$	$F_{AA, \text{block copolymer}}^b$
AA1	0	0.42	23.6	1.42	36.4	1.67	0.40
AA2	0	0.53	19.7	1.40	37.0	1.77	0.44
AA3	0	0.72	21.6	1.37	34.7	1.57	0.46
AA4	0	0.72	21.1	1.48	28.1	2.12	0.56
AA5	0.045	0.50	20.0	1.35	30.8	1.50	0.39
AA6	0.045	0.67	25.1	1.34	34.2	1.75	0.43
AA7	0.045	0.83	24.3	1.34	30.6	2.47	0.76
AA8	0.045	0.73	24.1	1.46	29.0	1.75	0.58
AA9	0.09	0.45	23.7	1.23	30.4	1.59	0.44
AA10	0.09	0.69	26.7	1.47	33.3	1.74	0.47
AA11	0.09	0.75	28.8	1.34	30.5	1.62	0.52
AA12	0.09	0.78	27.4	1.43	32.9	1.74	0.54

^a r = initial molar concentration of SG1 free nitroxide addition relative to initial molar concentration BlocBuilder[®] initiator = $[\text{SG1}]_0/[\text{BlocBuilder}]_0$

^b F_{AA} is the molar fraction of acrylic acid in the final polymer determined by ¹H nuclear magnetic resonance (NMR).

^cNumber average molecular weight ($\square$), weight average molecular weight ($\square$) and polydispersity index ($\square$) determined by gel permeation chromatography (GPC) relative to linear poly(styrene) standards in tetrahydrofuran (THF) at 40 °C.

Table 5. Molecular Weight Characterization of Poly(acrylic acid-*ran*-styrene)-Poly(styrene) (P(AA-*r*-S)-PS)) Block Copolymers at Various Polymerization Times Initiated by Poly(acrylic acid-*ran*-styrene) Copolymers at 120 °C in 50 wt% 1,4 Dioxane Solution.

Experiment ID ^a	time (min)	$\bar{M}_w$ (kg·mol ⁻¹)	$\bar{M}_w/\bar{M}_n$	Experiment ID ^a	time (min)	$\bar{M}_w$ (kg·mol ⁻¹)	$\bar{M}_w/\bar{M}_n$
AA1	0	30.1	1.54	AA7	0	26.1	1.39
	4	30.4	1.55		5	25.3	1.38
	11	32.9	1.51		20	25.8	2.49
	20	33.3	1.60		58	28.5	2.15
	30	33.8	1.64		103	30.6	2.47
	50	36.4	1.67		160	25.3	2.88
AA2	0	27.8	1.60	AA8	0	27.8	2.22
	6	29.9	1.62		5	27.1	2.05
	15	31.6	1.64		16	27.5	1.89
	30	33.7	1.72		30	27.2	1.77
	45	35.4	1.72		61	27.4	1.77
	60	37.0	1.77		102	29.0	1.75
AA3	0	25.7	1.55	AA9	0	22.1	1.82
	5	26.1	1.54		6	21.6	1.38
	15	28.9	1.53		16	23.8	1.40
	30	30.5	1.53		46	27.4	1.47
	45	32.2	1.57		76	29.2	1.54
	77	34.7	1.57		116	30.4	1.59
AA4	0	26.0	2.11	AA10	0	25.0	1.43

	5	24.4	2.19		5	25.0	1.49
	20	24.5	2.28		16	27.3	1.51
	50	27.3	2.11		30	29.4	1.56
	93	28.1	2.12		60	31.7	1.66
	122	27.9	2.41		90	33.4	1.74
AA5	0	23.2	1.45	AA11	0	27.0	1.45
	5	24.5	1.43		5	28.5	1.78
	16	25.9	1.43		21	28.5	1.51
	31	27.3	1.50		46	28.9	1.55
	45	28.9	1.48		92	30.0	1.61
	60	30.8	1.50		138	30.4	1.62
AA6	0	27.1	1.56	AA12	0	29.1	1.69
	16	29.2	1.65		5	30.3	2.04
	30	31.6	1.68		20	30.2	1.87
	45	34.2	1.75		60	31.4	1.70
	61	33.3	1.85		96	31.9	1.76
					128	32.9	1.74

^aExperiment ID refers to the experiments listed in Tables 1 and 4.

^bNumber average molecular weight ($\bar{M}_n$), weight average molecular weight ($\bar{M}_w$) and polydispersity index ($\bar{M}_w/\bar{M}_n$) determined by gel permeation chromatography (GPC) relative to linear poly(styrene) standards in tetrahydrofuran (THF) at 40 °C.

(Table 5 continued above)

Table 6. Experiments to Produce Poly(acrylic acid)-Poly(styrene) (PAA-PS) Diblock Copolymers from Various Poly(*tert*-butyl acrylate) (PtBuA) and Poly(styrene) (PS) Macroinitiators

ID	Macroinitiator			Intermediate polymer/initiator				Final PAA-PS copolymer		
	Form ^a	$\bar{M}_n^b$	PDI ^b	Form ^a	$\bar{M}_n^b$	PDI ^b	F_{tBuA}^c	$\bar{M}_n^b$	PDI ^b	F_{AA}^c
		(kg·mol ⁻¹)			(kg·mol ⁻¹)			(kg·mol ⁻¹)		
SA1	PtBuA	30.4	1.25	PtBuA-PS	47.6	1.47	0.59	48.5	1.54	0.59
SA2	PtBuA	30.4	1.25	PAA	25.3	1.33	-			
SA3	PS	32.0	1.18	PtBuA-PS	37.7	1.62	0.39	29.5	1.84	0.39
SA4	PS	32.0	1.18	-	-	-	-	41.8	2.58	0.62

^aForm refers to whether the polymer is in its homopolymer form such as poly(*tert*-butyl acrylate) (PtBuA), poly(styrene) (PS) or poly(acrylic acid) (PAA) or as a diblock such as PtBuA-PS.

^bNumber average molecular weight ($\bar{M}_n$), weight average molecular weight ($\bar{M}_w$) and polydispersity index (PDI) determined by gel permeation chromatography (GPC) relative to linear poly(styrene) standards in tetrahydrofuran (THF) at 40 °C.

^c F_{tBuA} is the molar fraction of *tert*-butyl acrylate in the final polymer as determined by ¹H NMR in CDCl₃ and F_{AA} is the molar fraction of acrylic acid in the final polymer as determined by ¹H NMR in deuterated acetone.

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Effect of Acid Protecting Group on “Livingness” of Poly(acrylic acid)/Poly(styrene) Random Copolymer Macroinitiators for Nitroxide-Mediated Polymerization of Styrene

Benoît Lessard and Milan Marić

