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Incorporating Primary Amine Pendant Groups into Copolymers via Nitroxide Mediated Polymerization

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Abstract

Primary amine incorporation as pendant groups on copolymers was studied via nitroxide mediated polymerization (NMP) using the BlocBuilder family of unimolecular initiators. When using the neat BlocBuilder initiator, a protected amine monomer, N-(t-BOCaminopropyl)methacrylamide (tBOC-MAm), was copolymerized with styrene (ST) at 110 °C or terpolymerized with ST and methyl methacrylate (MMA) at 90 °C. When copolymerized with ST, tBOC-MAm incorporation into copolymers was low compared to the feed composition, despite good control of the molecular weight distribution (polydispersity $\bar{M}_{w}/\bar{M}_{n}=1.25-1.34$). tBOC-MAm/MMA/ST terpolymerizations indicated better tBOC-MAm incorporation but high $\bar{M}_{w}/\bar{M}_{n} \sim 1.5$ -1.6 and poor "living character" (loss of linear number average molecular weight \overline{M}_n versus monomer conversion X relationship at X > 0.3 and poor ability to re-initiate a second batch of monomer). In contrast, using a protected form of BlocBuilder attached to oligomeric ST or MMA/STbased macroinitiators, feed compositions $f_{AST,0}$ containing 4-aminostyrene (AST) nonprotected monomer up to 0.10, resulted in good primary amine incorporation and linear M_n versus X up to X = 0.4. Higher $f_{AST,0}$ resulted in side-reactions and poorer control of the polymerization process. Thus, for the two primary amine monomers studied, in protected or non-protected forms, controlled polymerizations with good incorporation of amine-containing monomer are more readily approached when using AST in conjunction with a protected BlocBuilder-terminated oligomeric initiator, provided the AST feed composition is not excessively high.

Keywords: nitroxide mediated polymerization, statistical copolymerization, 4aminostyrene, protected amine monomers, methacrylamides.

1. Introduction

Controlled radical polymerization (CRP) has increasingly become a favourable route towards accessing polymers with narrow molecular weight distributions and well-defined microstructures for a wide range of applications such as optoelectronic materials [1], controlled release agents [2] and templates for separations media [3]. The popularity of CRP is derived largely from its ability to use conditions employed by conventional radical polymerization and the avoidance of extensive reagent purification, functional group protection and strictly air-free conditions employed by more traditional methods to obtain polymers with controlled microstructures (eg. "living" polymerizations). Variants of CRP have been developed such as reversible addition fragmentation transfer polymerization (RAFT) [4], atom transfer radical polymerization (ATRP) [5-7] and nitroxide mediated polymerization (NMP) [8], all of which use a reversible termination or chain transfer step to minimize irreversible termination reactions during a significant portion of the polymerization.

These variants have permitted the access to various functional polymers without resorting to protective chemistry. The importance of incorporating functional groups either as pendant groups or as terminal groups has been recognized widely. For example, primary amines, either attached to the chain end or pendent along the chain, are desirable for DNA vectors [9-11], stimuli-responsive materials [12], surface patterning [13] and as compatibilizers in polymer blends [14-17]. Various CRP methods have been applied to make polymers and copolymers with primary amine functionality. ATRP, by suitable functionalization of the bromide end group of the initiator to an azide and subsequent reduction, provided a primary amine at the chain terminus [18-20]. Suitably functionalized chain transfer agents for RAFT have been used to place primary amines onto the chain end [21, 22] while pendant amine functional polymers have also been directly synthesized by RAFT by suitable protection of the amine [23].

Incorporating primary amine containing monomers as pendant groups, without functional group protection, has been challenging, often due to solubility issues. Consequently, traditional conventional free radical polymerization approaches have relied on using bulk polymerization [24, 25], post-polymerization modification [26] or protective group chemistry [27] to directly incorporate pendant amine functionality into

the chain. CRP methods have generally tended to directly incorporate primary amines onto the chain end [28, 29] instead of as pendant groups [30-33]. Whether placing amines on the chain end or as pendant groups, the CRP methods used to incorporate amines were overwhelmingly based on ATRP and RAFT. Surprisingly, NMP has not been widely used to incorporate amine functionalities into polymers, despite its simple implementation (typically only initiator and heat is necessary) and its advantages compared to ATRP (NMP does not require removal of metallic impurities) and RAFT (NMP does not use odorous sulphur-based chain transfer agents). Advances in NMP initiators, however, open new possibilities for incorporation of amine groups into polymers/copolymers. Unimolecular initiators like BlocBuilder [34-38], TIPNO [39, 40] and more recently *N*-phenylalkoxyamines and related compounds [41-43] have enabled polymerization of acrylates and methacrylates which should widen the number of accessible polymers possessing amine functional groups at chain ends or along the length of polymer chains.

The following study aims to find NMP methods via BlocBuilder that could incorporate amine functional groups as pendant groups along a polymer chain. Specifically targeted here are protected/non-protected primary amine functional monomers that are commercially available and did not require further modification. Two methods were applied; one used a commercially available protected primary amine containing monomer, *N*-(*t*-BOC-aminopropyl)methacrylamide (*t*BOC-MAm), copolymerized with a hydrophobic monomer such as styrene (ST) or methyl methacrylate (MMA) (Scheme 1) while the other method used a protected initiator to directly incorporate a commercially available primary amine containing monomer, 4aminostyrene (Scheme 2). In its protected form, tBOC-MAm is organo-soluble and after copolymerization with ST or with MMA, mild treatment with acid will remove the *t*BOC protecting group and yield a copolymer with random primary amine functionality. When incorporating directly the primary amine using 4-aminostyrene (AST), protecting the BlocBuilder initiator's carboxylic acid functionality was necessary. Using the method of Vinas et al [44] to convert the BlocBuilder to an *N*-hydroxysuccinimide terminated form (NHS-BlocBuilder), oligomers were synthesized and subsequently protected by a suitable monoamine reaction. The protected oligomers were then used as macroinitiators for the controlled radical copolymerization of ST/AST and MMA/AST mixtures. The results of this study are intended to determine the capabilities of the two aforementioned BlocBuilder-based routes to incorporate pendant primary amine groups into well-defined copolymers using NMP.

2. Experimental

2.1. Materials

Styrene (ST, 99%), methyl methacrylate (MMA, 99%) monomers were obtained from Aldrich and had their inhibitors removed by passage through a column of basic alumina (Al₂O₃, Brockman Type I, 150 mesh, Aldrich) and calcium hydride (90-95%, Aldrich) (95% by weight Al₂O₃). Benzylamine and N-hydroxy succinimide (NHS) were obtained from Aldrich and used as received. 4-aminostyrene (AST) was acquired from Oakwood Chemicals and used as received. N-(t-BOC-aminopropyl)methacrylamide (tBOC-MAm) was used as received from Polysciences. Dioxane (99.5%), tetrahydrofuran (THF, 99.5%) and hexane (99.5%) were acquired from Fisher and used The as received. alkoxyamine unimolecular initiator, 2(-{*tert*-buty[1diethoxyphosphoryl)2,2-dimethylpropyl]amino}oxy-2-methylpropanoic acid (BlocBuilder, 99%) was obtained from Arkema and used as received and the free nitroxide, {tert-butyl[1-(diethoxyphosphoryl)-2,2-dimethylpropyl]amino}oxidanyl, (SG1, 85%) was kindly provided by Noah Macy of Arkema and used as received. Deuterated chloroform (CDCl₃, > 99%, Cambridge Isotopes Laboratory) was used as a solvent for proton nuclear magnetic resonance (¹H NMR).

2.2. Styrene/N-(t-BOC-aminopropyl)methacrylamide) copolymerization

The reactor was a three-necked 50 mL round bottom flask equipped with a magnetic stirrer and a heating mantle/controller. To one neck was attached a condenser that was cooled to 5 °C by an ethylene glycol/water mixture recirculating chiller (Neslab). The condenser was capped by a rubber septum with a needle to serve as an outlet for the nitrogen purge used. To another port was connected a thermal well attached to the temperature controller. The third port of the reactor was sealed with a rubber septum and was connected via a needle to a tank of ultra-pure nitrogen that supplied the purge to

remove all oxygen from the reactor. The number average molecular weight assuming complete conversion ($\overline{M}_{n \text{ target}}$) was set to 20 kg mol⁻¹. An example is given for sample ST-tBOC-MAm-20 (see Table 1 for all ST/tBOC-MAm copolymerizations with BlocBuilder/SG1). The solvent, 1,4 dioxane (6.78 g), was first added to the reactor followed by BlocBuilder (0.11 g), SG1 (0.0075 g) and previously purified styrene monomer (4.89 g). Then the solid monomer, tBOC-MAm (1.98 g), was added carefully to the reactor and the reactor was sealed and the nitrogen purge was started for 30 minutes. Then, the reactor temperature was increased to 110 °C at a rate of about 10 °C min⁻¹. When the temperature reached 100 °C, the polymerization time was taken as the initial time. Samples were periodically removed and precipitated in hexane. The aliquots were left to settle for several hours before the supernatant was decanted. The aliquots were then re-dissolved in THF and precipitated once more with hexane. After cooling in a refrigerator for 30 minutes, the supernatant was once again decanted, filtered under vacuum and the aliquots were then placed in a vacuum oven overnight at 60 °C to thoroughly dry the samples. The final yield was 1.0 g (conversion = 15%) and the copolymer $\bar{M}_n = 11.3 \text{ kg} \cdot \text{mol}^{-1}$ and polydispersity index = $\bar{M}_w / \bar{M}_n = 1.28$ according to gel permeation chromatography (GPC) relative to linear poly(styrene) standards in THF. The copolymer molar composition was $F_{tBOC-MAm} = 0.10$ according to ¹H NMR in CDCl₃: $\delta = 7.8$ ppm (t, 1H, -CO-NH-CH₂), $\delta = 6.7$ ppm (t, 1H, -CH₂-NH-COO-), $\delta = 6.7$ ppm (m, 2H, aromatic), $\delta = 7.2$ ppm (m, 3H, aromatic), $\delta = 3.1$ ppm (t, 2H, -CO-NH- CH_2 -CH₂-), $\delta = 2.9$ ppm (t, 2H, -CH₂-CH₂-NH-COO-), $\delta = 1.9$ ppm (s, 3H, CH₂-CH- CH_{3} -), $\delta = 1.5$ ppm (m, 2H, -CH₂-CH₂), $\delta = 1.3$ ppm (s, 9H, COO-C-(CH₃)₃), $\delta =$ 1.0-1.7 ppm (backbone aliphatic protons).

2.3. *Methyl methacrylate/styrene/N-(t-BOC-aminopropyl)methacrylamide)* (MMA/ST/tBOC-MAm) nitroxide mediated terpolymerization

Similar reaction conditions were used for the MMA/ST/tBOC-MAm terpolymerizations as for the ST/tBOC-MAm binary copolymerizations. $\overline{M}_{n, targel}$ of the terpolymer was identical to the ST/tBOC-MAm copolymer. An example is given below for sample ST-MMA-tBOC-MAm-20. All terpolymerization formulations are summarized in Table 2. The solvent, 1,4 dioxane (5.77 g), was first added to the reactor

followed by BlocBuilder (0.10 g), SG1 (0.0075 g), previously purified ST (0.39 g) and MMA (3.33 g). Then the solid monomer, tBOC-MAm (2.10 g), was added carefully to the reactor and the reactor sealed and nitrogen purge commenced. After 30 minutes, the reactor temperature was increased to 90 °C at a rate of about 10 °C min⁻¹. When the temperature reached 80 °C, the polymerization time was taken as the initial time. Samples were periodically removed and precipitated in hexane. The aliquots were left to settle for several hours before the supernatant was decanted. The aliquots were then redissolved in THF and precipitated once more with hexane. After cooling in a refrigerator for 30 minutes, the supernatant was once again decanted, filtered under vacuum and the aliquots were then placed in a vacuum oven overnight at 60 °C to thoroughly dry the samples. The final yield was 2.65 g with $\bar{M}_n = 8.2 \text{ kg} \cdot \text{mol}^{-1}$ and $\bar{M}_w / \bar{M}_n = 1.49$ according to gel permeation chromatography (GPC) relative to linear poly(styrene) standards in THF. The terpolymer molar composition relative to tBOC-MAm and MMA were $F_{tBOC-MAm} = 0.09$ and $F_{MMA} = 0.80$ according to ¹H NMR in CDCl₃: $\delta = 7.8$ ppm (t, 1H, -CO-NH-CH₂), $\delta = 6.7$ ppm (t, 1H, -CH₂-NH-COO-), $\delta = 6.7$ ppm (m, 2H, aromatic), $\delta = 7.2$ ppm (m, 3H, aromatic), $\delta = 3.8$ ppm (s, 3H, COO-CH₃), $\delta = 3.1$ ppm (t, 2H, -CO-NH-CH₂-CH₂-), $\delta = 2.9$ ppm (t, 2H, -CH₂-CH₂-NH-COO-), $\delta = 1.9$ ppm (s, 3H, CH₂-CH-CH₃-), $\delta = 1.8$ ppm (s, 3H, CH₂-CH-CH₃), $\delta = 1.5$ ppm (m, 2H, -CH₂-CH₂-CH₂), $\delta = 1.3$ ppm (s, 9H, COO-C-(CH₃)₃), $\delta = 1.0-1.7$ ppm (backbone aliphatic protons).

2.4. Chain extension polymerizations of N-(t-BOC-aminopropyl)methacrylamide) (tBOC-MAm)-containing macroinitiators

Testing of the ability of the various *t*BOC-MAm containing copolymers or terpolymers to successfully initiate a second batch of monomer was also undertaken. All the formulations for the chain extensions are summarized in Table 3. The reactor set-up was identical to those of the copolymerizations described above. Typically for the case of ST-*t*BOC-MAm macroinitiators, using ST-*t*BOC-MAm-20 as a macroinitiator, 0.61 g of macroinitiator was added to the reactor containing 3.08 g of monomer (styrene) and 3.21 g of 1,4 dioxane solvent. The reactor was set up as previously described in the Section 2.2 above. After sealing the reactor, a nitrogen purge was applied for 30 minutes at ambient conditions to degas the mixture. Then, the reactor temperature was increased

at a rate of 10 °C min⁻¹ up to 110 °C. When the temperature reached 100 °C, the polymerization time was taken as the initial time for the chain extension. For the chain extensions done with styrene, samples were periodically removed and precipitated into excess methanol. The product was filtered, re-dissolved in THF and precipitated once more into methanol and filtered once again. The product was then placed in a vacuum oven at 60 °C overnight to remove the last traces of monomer and solvent. The final yield was 1.74 g with $\bar{M}_n = 34.0 \text{ kg} \cdot \text{mol}^{-1}$ and $\bar{M}_w / \bar{M}_n = 2.00$ according to gel permeation chromatography (GPC) relative to poly(styrene) standards in THF. The molar composition was FtBOC-MAM = 0.018 according to ¹H NMR in CDCl₃.

A similar procedure was used when using the ST-MMA-tBOC-APMAm terpolymers as macroinitiators for the chain extensions with MMA/ST. Using ST-MMAtBOC-30 as an example, 1.01 g of ST-MMA-tBOC-30 was dissolved in 6.01 g of dioxane and then 4.57 g of MMA and 0.53 g of ST were added and followed by reactor sealing and nitrogen purging for 30 minutes. The reactor temperature was increased to 90 °C at a rate of about 10 °C min⁻¹. For the MMA/ST chain extensions, samples were periodically removed and precipitated into hexane to recover the product. The product was filtered, re-dissolved in dioxane and precipitated once more into hexane and then recovered by filtration and dried in a vacuum oven at 60 °C overnight. The final yield was 1.4 g with $\bar{M}_n = 11.8 \text{ kg} \cdot \text{mol}^{-1}$ and $\bar{M}_w / \bar{M}_n = 1.68$ according to gel permeation chromatography (GPC) relative to poly(styrene) standards in THF. The copolymer molar composition was $F_{tBOC-MAm} = 0.19$, $F_{MMA} = 0.57$ according to ¹H NMR in CDCl₃: $\delta = 7.8$ ppm (t, 1H, -CO-NH-CH₂), $\delta = 6.7$ ppm (t, 1H, -CH₂-NH-COO-), $\delta = 6.7$ ppm (m, 2H, aromatic), $\delta = 7.2$ ppm (m, 3H, aromatic), $\delta = 3.8$ ppm (s, 3H, COO-CH₃), $\delta = 3.1$ ppm (t, 2H, -CO-NH-CH₂-CH₂-), $\delta = 2.9$ ppm (t, 2H, -CH₂-CH₂-NH-COO-), $\delta = 1.9$ ppm (s, 3H, CH₂-CH-CH₃-), $\delta = 1.8$ ppm (s, 3H, CH₂-CH-CH₃), $\delta = 1.5$ ppm (m, 2H, -CH₂-CH₂-CH₂), $\delta = 1.3$ ppm (s, 9H, COO-C-(CH₃)₃), $\delta = 1.0-1.7$ ppm (backbone aliphatic protons).

2.5. N-hydroxysuccimidyl terminated poly(styrene) oligomer

N-hydroxysuccimimide (NHS) was reacted with BlocBuilder to protect the carboxylic acid, as described in the literature [44]. The NHS-terminated BlocBuilder

(termed NHS-BlocBuilder hereafter) was then used initiate styrene to homopolymerization at 110 °C to produce an NHS-terminated poly(styrene) oligomer. Using the same reactor apparatus and set-up as described above, 0.40 g of NHS-BlocBuilder and 12.6 g of styrene were added to the reactor followed by purging for 30 minutes at ambient conditions. The contents were then heated up 110 °C and the reaction was allowed to proceed for 2 h, and then cooled. The contents were then poured into excess methanol to precipitate the polymer. After vacuum filtration and drying at 60 °C overnight in a vacuum oven, a low molecular weight PS-NHS oligomer was recovered $(\bar{M}_n = 3.1 \text{ kg·mol}^{-1}, \bar{M}_w/\bar{M}_n = 1.16, \text{ yield} = 1.7 \text{ g, conversion} = 0.15)$ for use as a macroinitiator for ST/AST copolymerization. The PS-NHS oligomer (1.0 g) was then dissolved in 20 mL of dry methylene chloride at 4 °C and bubbled with nitrogen gas before adding 10x molar excess of benzylamine (0.38 mL). The reaction was performed for 4 h at 4 °C. The contents were then precipitated into methanol to remove unreacted benzylamine and N-hydroxysuccinimide and to isolate the benzylamide terminated PS oligomer (PS-BzAm). After vacuum filtration and drying in a vacuum oven overnight at 60 °C, 0.76 g of the PS-BzAm was recovered ($\overline{M}_n = 3.6 \text{ kg·mol}^{-1}, \overline{M}_w / \overline{M}_n = 1.11$).

2.6. N-hydroxysuccimide terminated poly(methyl methacrylate-ran-styrene) oligomer

The NHS-terminated BlocBuilder was also used to initiate MMA/ST copolymerization at 90 °C to produce an NHS-terminated poly(MMA-*r*-ST) oligomer. 0.51 g of NHS-BlocBuilder, 1.31 g of ST, 14.4 g of MMA and 15.7 g of dioxane solvent were added to the same reactor apparatus as described above. After nitrogen purging for 30 minutes, the reactor was then heated up to 90 °C for 1 h before being cooled. The contents were then poured into an excess of hexane. The polymer was recovered by vacuum filtration and the crude polymer was dried at 70 °C in a vacuum oven overnight. The resulting P(MMA-*r*-ST)-NHS oligomer yield was 3.19 g (\overline{M}_n = 5.8 kg·mol⁻¹, $\overline{M}_w/\overline{M}_n$ = 1.39). This was then converted for use as a macroinitiator for MMA/4-aminostyrene copolymerization. The P(MMA-*r*-ST)-NHS oligomer (1.01 g) was then dissolved in 20 mL of dry methylene chloride at 4 °C in a sealed round bottom flask and bubbled with nitrogen gas for 15 minutes. Then, a 10x molar excess of benzylamine (0.10 mL) was injected via syringe. The reaction was performed for 4 h. The contents

were then precipitated into hexane to remove unreacted benzylamine and *N*-hydroxysuccinimide and to isolate the benzylamide terminated P(MMA-*r*-ST) oligomer (P(MMA-*r*-ST)-BzAm). After placing in in a vacuum oven at 70 °C to remove unreacted monomer and solvent, a yield of 0.75 g resulted ($\overline{M}_n = 6.4 \text{ kg} \cdot \text{mol}^{-1}$, $\overline{M}_w / \overline{M}_n = 1.32$, F_{MMA} = 0.91). ¹H NMR, CDCl₃: $\delta = 6.7$ -7.2 ppm (m, 5H, aromatic), $\delta = 3.8$ ppm (s, 3H, COO-CH₃), $\delta = 1.9$ ppm (s, 3H, -CH₂-CH-CH₃-), $\delta = 1.0$ -1.7 ppm (backbone).

2.7. Poly(styrene)-block-poly(styrene-ran-4-aminostyrene) copolymers

The PS-BzAm oligomer ($\bar{M}_n = 3.6 \text{ kg} \cdot \text{mol}^{-1}$, $\bar{M}_w / \bar{M}_n = 1.11$) was used to initiate the statistical copolymerization of ST and AST at 110 °C in 50 wt% dioxane solution. The same reactor set-up was applied as for the polymerizations described in previous sections. 0.25 g of PS-BzAm was added to 2.75 of dioxane followed by 0.28 g of AST and 2.22 g of previously purified ST (monomer feed content was 10 mol% AST). The contents were bubbled with nitrogen for 30 minutes at room temperature and then the reactor was heated to 110 °C. Samples were withdrawn periodically for molecular weight determination. After 6 h, the reaction was stopped by cooling and precipitating the contents into hexane. The product was placed in a vacuum oven at 60 °C to remove unreacted monomer and solvent. 0.76 g of product resulted with $\bar{M}_n = 19.5 \text{ kg} \cdot \text{mol}^{-1}$ and $\bar{M}_w / \bar{M}_n = 1.36$. According to ¹H NMR in CDCl₃, the composition of the particular copolymer with respect to AST was $F_{AST} = 0.16$. ¹H NMR, CDCl₃: $\delta = 6.7$ -7.2 ppm (m, 4H from AST, 5H from ST, aromatic). $\delta = 3.7 \text{ ppm}$ (s, 2H, -C₆H₄-NH₂), $\delta = 1.0$ -1.7 ppm, backbone).

2.8. Poly(methyl methacrylate-ran-styrene)-block-poly(methyl methacrylate-ran-4aminostyrene) copolymers

The P(MMA-*r*-ST)-BzAm oligomer was used to initiate the statistical copolymerization of MMA and AST at 90 °C in 50 wt% dioxane solution for two different batch compositions. The same reactor set-up was applied as for the polymerizations described in previous sections. The example given is for a feed composition of 10 mol% AST with MMA. To the reactor was added 0.37 g of P(MMA-

r-ST)-BzAm ($\bar{M}_n = 6.4 \text{ kg} \cdot \text{mol}^{-1}$, $\bar{M}_w / \bar{M}_n = 1.32$, $F_{\text{MMA}} = 0.91$) followed by 4.07 g of dioxane solvent, 0.47 g of AST and 3.46 g of MMA previously purified. The contents were bubbled with nitrogen for 30 minutes at room temperature and then the reactor was heated to 90 °C. Samples were withdrawn periodically for molecular weight and conversion determination. After 1 h, the reaction was stopped by cooling and precipitating the contents into hexane. The product was placed in a vacuum oven at 70 °C to remove unreacted monomer and solvent. 0.87 g of product resulted with $\bar{M}_n = 19.5 \text{ kg} \cdot \text{mol}^{-1}$ and $\bar{M}_w / \bar{M}_n = 1.36$. The copolymer composition with respect to MMA, F_{MMA} , was 0.87. ¹H NMR, CDCl₃: $\delta = 6.7$ -7.2 ppm (m, 5H, aromatic), $\delta = 3.8$ ppm (s, 3H, COO-CH₃), $\delta = 3.7$ ppm (s, 2H, -C₆H₄-NH₂), $\delta = 1.9$ ppm (s, 3H, -CH₂-CH-CH₃-), $\delta = 1.0$ -1.7 ppm (backbone).

2.9. Characterization

Overall monomer weight conversions were determined gravimetrically. These conversions were used in plots involving molecular weight and polydispersity index versus conversion. Kinetic plots (those involving conversion versus time) should be based on molar conversions. A similar approach was used by Charleux and co-workers for styrene/acrylic acid copolymerization controlled by an SG1-type initiator [45]. In cases where the monomers in the copolymerization had very similar molecular weights, these conversions could be used almost interchangeably. Molecular weights (number average molecular weight \overline{M}_n , weight average molecular weight \overline{M}_w and polydispersity index \bar{M}_w/\bar{M}_n were estimated using gel permeation chromatography (GPC, Waters Breeze) with THF as the mobile phase at a flow rate of 0.3 mL min⁻¹. The GPC was equipped with a guard column and 3 columns for separation (Waters Styragel® HR series). The specific columns used were HR1 (molecular weight measurement range of $10^2 - 5 \times 10^3$ g mol⁻¹), HR2 (molecular weight measurement range of $5 \times 10^2 - 2 \times 10^4$ g mol⁻¹) and HR4 (molecular weight measurement range of 5 x $10^3 - 6$ x 10^5 g mol⁻¹). The columns were kept at 40 °C during the analysis and the molecular weights were estimated relative to linear poly(styrene) standards. The GPC was equipped with both differential refractive index (RI 2410) and ultraviolet (UV 2487) detectors for which the RI detector

was used solely for the experiments described herein. For the samples with AST units, the amine groups were quenched with phenyl isocyanate to prevent the amine groups from adhering to the columns.

¹H NMR measurements were done with a 200 MHz Varian Gemini 2000 spectrometer using CDCl₃ solvent in 5 mm Up NMR tubes. The samples were scanned at least 64 times after injection and shimming. Copolymer composition was determined by integrating the resonances unique to each monomer. For tBOC-MAm, the resonances of interest are as follows: $\delta = 1.3$ ppm (s, 9H, COO-C-(CH₃)₃), $\delta = 1.5$ ppm (m, 2H, -CH₂- CH_2 -CH₂), $\delta = 1.8$ ppm (s, 3H, C-CH₃), $\delta = 2.9$ ppm (t, 2H, -CH₂-CH₂-NH-COO-), $\delta =$ 3.1 ppm (t, 2H, -CO-NH-CH₂-CH₂-), $\delta = 6.7$ ppm (t, 1H, -CH₂-NH-COO-), $\delta = 7.8$ ppm (t, 1H, -CO-NH-CH₂) and the backbone resonances at $\delta = 1.0-1.7$ ppm. For ST, the resonances of interest are as follows: $\delta = 6.7$ ppm (m, 2H, aromatic) and $\delta = 7.2$ ppm (m, 3H, aromatic) in addition to the backbone resonances at $\delta = 1.0-1.7$ ppm. For MMA, the resonances of interest are as follows: $\delta = 1.9$ ppm (s, 3H, -CH₂-CH-CH₃-) and $\delta = 3.8$ ppm (s, 3H, COO-CH₃) in addition to the backbone resonances at $\delta = 1.0-1.7$ ppm. For AST, the resonances are $\delta = 3.7$ ppm (s, 2H, -C₆H₄-NH₂) $\delta = 6.7$ ppm (m, 2H, aromatic) and $\delta = 7.2$ ppm (m, 2H, aromatic) in addition to the backbone resonances at $\delta = 1.0-1.7$ ppm. Specifically, for ST/tBOC-MAm copolymer compositions, the signal due to the three aromatic protons corresponding to ST ($\delta = 7.2$ ppm) were compared to either the signals at $\delta = 2.9$ ppm and 3.1 ppm (corresponding to 2 protons each) that are unique to tBOC-MAm. For the ST/MMA/tBOC-MAm terpolymers, the signals used for composition determination were: $\delta = 7.2$ ppm (3H, ST), $\delta = 3.8$ ppm (3H, MMA) and $\delta =$ 3.1 ppm (2H, *t*BOC-MAm).

3. Results and Discussion

3.1. Polymerization of protected amine-containing monomer with neat BlocBuilder unimolecular initiator

The binary copolymerization of ST with *t*BOC-MAm at 110 °C was first studied in 50 wt% dioxane solution using BlocBuilder initiator and ~ 9-10 mol% additional SG1 free nitroxide relative to BlocBuilder. These initial experiments indicated that *t*BOC-MAm does not greatly affect the polymerization rate in the feed composition range studied, as the yield after about 3 h was not appreciably greater than that of styrene at the same temperature. This is in agreement with other related controlled radical systems using acrylamides [27-30] and methacrylamides [33-36] that do not seem to polymerize significantly faster than styrenic monomers. Table 4 summarizes the molecular properties of the ST/*t*BOC-MAm copolymers. In all cases, the molecular weight distributions were quite narrow and monomodal, with $\overline{M}_{w}/\overline{M}_{n} = 1.25-1.34$.

For the tBOC-MAm/ST binary system, incorporation of the tBOC-MAm into the copolymer, $F_{tBOC-MAm}$, was lower than that of the feed composition, $f_{tBOC-MAm}$ (Table 4). Indeed, at the lowest feed composition, ¹H NMR detected virtually no *t*BOC-MAm in the copolymer. The $F_{lBOC-MAm}$ suggest that the reactivity ratios for this particular binary system are such that $r_{tBOC-MAm} \ll 1$ and $r_{ST} > 1$ (ST prefers to add on to another ST unit much more than to a *t*BOC-MAm unit). No literature data is available for reactivity ratios between ST and tBOC-MAm using either conventional radical polymerization or controlled radical polymerization. For comparison, ST/methacrylamide (MAAm) conventional radical polymerizations performed in dioxane over a ST feed composition range $f_{ST,0} = 0.29-0.965$ (six compositions) reported reactivity ratios of $r_{ST} = 2.89$ and $r_{MAAm} = 2.04$ [46]. Erceg et al performed ST/N-(p-phenoxy-phenyl) methacrylamide (PhOPhMAA) conventional radical copolymerizations from $f_{ST,0} = 0.3-0.8$ (six compositions) in toluene at 70 °C and reported nearly statistical copolymerizations with $r_{ST} = 0.61$ and $r_{PhOPhMAA} = 0.55$ [47]. Covolan et al. reported ST conventional radical polymerizations with a tBOC protected p-aminostyrene (tBOC-AST) to be "quasirandom" in microstructure with $r_{ST} = 0.47$ and $r_{tBOC-AST} = 0.96$ [27]. The difficulties in incorporating tBOC-MAm suggested alternative methods to incorporate the desired functionality were necessary. Consequently, our attention was focused upon methacrylic copolymerizations that may help incorporate the tBOC-MAm to higher levels in the copolymers. ST/MMA/MAAm conventional radical terpolymerizations revealed slightly more preferential ST and MMA incorporation into the terpolymer compared to MAAm, but the incorporation was much more efficient compared to our results with the ST/*t*BOC-MAm binary copolymerization [48].

The terpolymerization of ST with MMA and *t*BOC-APMAm were synthesized using BlocBuilder/SG1 (with ~ 9 mol% SG1 relative to BlocBuilder to ensure good control of the predominantly methacrylic feeds) in 50 wt% dioxane solution at 90 °C. ST was used at low feed concentrations ~ 8 mol% in order to keep the polymerization controlled as has been shown previously when using BlocBuilder to polymerize methacrylic monomers [22]. The slope of the semi-logarithmic plots of $\ln[1/(1-X)]$ (X =conversion) versus polymerization time t, k_p [P·], where k_p is the propagation rate constant and [P·] is the concentration of propagating polymeric radicals, can be converted to the quantity k_pK , where K is the equilibrium constant between the propagating chains and the dormant, SG1-capped chains [35, 37, 38]. Implicit in this estimate of k_pK is the assumption that no significant irreversible termination reactions are occurring and the chains are substantially capped with SG1 groups. The relationship between the apparent rate constant k_p [P·] and k_pK is provided by Equation 1 below.

$$k_{p}K = k_{p} \frac{\left[P \cdot\right]\left[SG1\right]}{\left[P - SG1\right]} \cong k_{p} \frac{\left[P \cdot\right]\left[SG1\right]_{0}}{\left[BlocBuilder\right]_{0}} = k_{p}\left[P \cdot\right]r$$
^[1]

Note that [SG1] is the concentration of free nitroxide and [P-SG1] is the concentration of the dormant SG1-capped chains. In the linear region of the plots (during the early stages of the polymerization), the concentration of free nitroxide is initially high and does not change significantly in the early stages of the polymerization so that [SG1] \approx [SG1]₀. Also, the concentration of polymer chains is approximated by the initial concentration of initiator so that [P-SG1] \approx [BlocBuilder]₀. In our case, such assumptions are difficult to apply as the conversion leveled off quite early during the polymerization. Therefore, estimates of $k_p K$ were not reliable. Variation of the tBOC-MAm in the feed did not however strongly influence the polymerization rates and our yields were not significantly different from reported $k_p K$ (90 °C) for MMA/ST (~8 mol% ST in the feed) ~ 1 x 10⁻⁵ s⁻¹ [23].

The molecular weight distributions were broader for the MMA/ST/tBOC-MAm terpolymers compared to the ST/tBOC-MAm copolymers (Table 5). The plot of \overline{M}_{n} versus conversion for the terpolymerization shown in Fig. 1 indicated a plateau at higher conversions, suggestive of irreversible termination. This is suggestive of some type of chain transfer, perhaps β -H abstraction, which is common in methacrylic systems [20]. It was also noticed that the solution became progressively more yellow during the course of the terpolymerization, indicating more free nitroxide being liberated as termination reactions were occurring. We have noticed a similar color change in acrylic acid/styrene copolymerizations mediated by BlocBuilder [49-50], which is due to hydroxylamine formation from the attack of the organic acid on the nitroxide [51]. The NMP of tert-butyl acrylamide (TBAm) with SG1 also showed a levelling in the \overline{M}_n versus conversion plot, suggestive of chain transfer to monomer or solvent [52]. The latter authors found that chain transfer to monomer was dominant and that the *tert*-butyl substituent of TBAm was responsible for the chain transfer. However, it may be possible that the protons from the amide groups on the tBOC-AMPAm were interacting with the nitroxide, since acrylamide monomers such as N,N dimethylacrylamide (DMAm) [53-56] and N,N diethylacrylamide (DEAm) [57] that do not have a proton on the nitrogen, resulted in well-controlled polymerizations with SG1-based initiators. In contrast, monomers such as N-isopropylacrylamide (NIPAM) have been found to be more difficult to control by NMP. For example, NIPAM/TBAm copolymerizations were controlled and living up to low monomer conversions $\sim 15\%$ using SG1-based initiators [58]. NIPAM homopolymerization is challenging to polymerize in a controlled manner with SG1-based nitroxides and recent efforts using sterically hindered nitroxides have been more effective at controlling NIPAM homopolymerizations with nitroxides [59-60].

To see if the ST/tBOC-MAm and MMA/ST/tBOC-MAm were substantially terminated, chain extension experiments with a second batch of fresh monomer were done (i.e. testing of so-called "living character"). "Living character" was defined here if the number average molecular weight \overline{M}_n versus conversion increases linearly while maintaining a relatively narrow, monomodal molecular weight distribution. Based on the GPC chromatograms shown in Fig. 2, the ST/tBOC-MAm was sufficiently living as very

little macroinitiator was left unreacted. Thus, styrenic block copolymers where one segment has some protected primary amine units are accessible via the NMP conditions described here, although the incorporation the protected primary amine monomer was low in the macroinitiator. In the case of the MMA/ST/*t*BOC-MAm terpolymerizations, samples taken during various times of the chain extension would show if any dead macroinitiator was present. Fig. 3 shows the chain extensions from each of the terpolymer macroinitiators possessing different concentrations of *t*BOC-APMAm. For each of the macroinitiators, there was a high fraction of dead macroinitiator chains, suggesting that irreversible termination reactions were occurring during the synthesis of the macroinitiator, as suggested by our observations in Fig. 1. Indeed, the peaks did not move shift significantly at all, as the molecular weights of the chain-extended species were not much higher compared to the macroinitiators (Table 6).

3.2. Polymerization of non-protected primary amine-containing monomer with protected BlocBuilder unimolecular initiator

Thus, the use of the protected primary amine monomer in NMP with BlocBuilder possessed several drawbacks, based on our observations with the use of the *t*BOC-MAm. In the case of the ST/*t*BOC-MAm copolymerizations, incorporation of the *t*BOC-MAm was quite inefficient compared to the feed composition. When making primarily methacrylic terpolymers with *t*BOC-MAm, molecular weight distributions were broader compared to the ST/*t*BOC-MAm copolymerization, and suffered from a distinct lack of living character. Thus, the ability to form block copolymers with the commercially available *t*BOC-MAm monomer in one segment was not straightforward. Consequently, alternative methods using BlocBuilder were studied to see if incorporation of the amino functional monomer could be done easily and allow for the flexibility to make block copolymers.

The NHS-protection of the BlocBuilder followed by the synthesis of NHSterminated poly(styrene) oligomer was a contrasting method to place the primary amine functional monomer into a poly(styrene). Here, the initiator was further protected by reacting the poly(styrene)-NHS terminated oligomer with benzylamine (PS-BzAm). This oligomer was then used as a macroinitiator for a batch of ST and the primary amine

functional 4-aminostyrene, AST. The kinetics and the livingness plots revealed interesting trends regarding the incorporation of AST. The kinetic plots revealed that the propagation rate slowed as the feed composition of AST increased (Fig. 4). The \overline{M}_{n} versus conversion plots in Fig. 5 reveal that using a feed composition of $f_{AST,0} = 0.10$ resulted in a linear increase of \overline{M}_n with monomer conversion up to about X = 0.4 before a plateau started to become visible, suggesting the onset of irreversible termination reactions. The molecular weight distributions were monomodal and started to only get broader at high conversion. This suggests that the PST-BzAm macroinitiator was quite effective at initiating a batch of ST/AST monomers with an AST feed concentration of $f_{AST,0} = 0.10$. At $f_{AST,0} = 0.30$, the \overline{M}_n versus conversion plot was not linear and strongly indicated a plateau with the \overline{M}_n not changing much after X > 0.20. This is indicative of side-reactions occurring as suggested by Covolan et al. [27] when AST was used as a comonomer for a conventional radical polymerization. These authors stated that protection of the amino group was necessary to reduce the possibility of transfer of the lone electron pair to the vinyl group of the monomer. However, here we were able to incorporate enough primary amine functionality into the block copolymer so that it would be useful in many applications, particularly reactive blending where only a low concentration of amine groups is necessary.

The incorporation of the primary amine containing monomer into predominantly methacrylic resins was also done. First, the MMA-rich macroinitiator was synthesized using the protected initiator, NHS-BlocBuilder. The polymerization was stopped at relatively low conversion to ensure good livingness of the resulting poly(MMA-*r*-ST) macroinitiator. Also of note is that no additional free nitroxide was used in the polymerization of the macroinitiator, as what was required previously for methacrylate-rich feeds to ensure sufficient control of the polymerization [61]. The resulting copolymer possessed a narrow, monomodal molecular weight distribution ($\overline{M}_n = 5.8$ kg·mol⁻¹, $\overline{M}_w/\overline{M}_n = 1.39$). This control was expected due to the high dissociation rate constant of the NHS-BlocBuilder measured by electron spin resonance (ESR), which ensured an excess of free nitroxide at very early stages of the polymerization [44]. To ensure that the NHS-functionality on the terminus of the poly(MMA-*r*-ST) chain would

not react with the AST, the poly(MMA-r-ST) was treated with benzylamine postpolymerization. The resulting treated MMA-rich copolymer (sample ID = P(MMA-r-ST)-BzAm, $\overline{M}_n = 6.2 \text{ kg} \cdot \text{mol}^{-1}$, $\overline{M}_w / \overline{M}_n = 1.33$, $F_{MMA} = 0.91$) was then used to initiate polymerizations of MMA/AST batches with different concentrations of AST. In both cases, there was a clear shift from the macroinitiator to the chain-extended species evident from the GPC traces, with very little dead macroinitiator remaining (Fig. 6). The chain-extended species possessed a monomodal molecular weight distribution, with only a slight tailing evident. This may be due to some absorption of the amine-containing species onto the column, despite the solution being treated with phenyl isocyanate to quench the amine groups prior to analysis. Further, using AST as the co-monomer for the NMP of MMA did not lead to a dramatic loss in control of the polymerization, and thus behaves similarly to other styrenic monomers as controller for methacrylate-rich copolymerizations via BlocBuilder controlled NMP. However, as is noticed in Fig. 6b, the polymerization seems to have halted, suggesting the higher concentration of AST may have led to inhibitory side reactions as suggested by Covolan et al. [27] We are now examining in more detail how functional monomers can be cleanly incorporated into methacrylic-rich resins using the macroinitiator method described above.

4. Conclusions

Two different methods based on BlocBuilder NMP were compared to place primary amine groups as pendant functionalities into ST and MMA-rich copolymers. Using a protected amine monomer, *t*BOC-MAm, with the non-protected carboxylic acid functional BlocBuilder initiator was not desirable for two reasons. For ST-rich feeds, although molecular weight distributions were relatively narrow, low incorporation of *t*BOC-MAm relative to the feed composition was observed. For MMA/ST/*t*BOC-MAm terpolymerizations, incorporation of *t*BOC-MAm was better compared to the ST/tBOC-MAm copolymerizations, but the resulting poly(MMA-*r*-ST-*r*-*t*BOC-MAm) did not effectively initiate a second batch of monomer. Protecting the BlocBuilder initiator and using a non-protected primary amine monomer, AST, was the contrasting method to place primary amines along the polymer chain. From either poly(ST) or poly(MMA-*r*-ST) macroinitiators, chain extensions with AST-containing mixtures were relatively well-

controlled using feeds containing up to 10 mol% AST. At higher AST feed concentrations, side-reactions were becoming prevalent, as evidenced by a limit to the molecular weight attainable.

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7. Fig. captions

Scheme 1. Polymerizations used to derive pendant amine functional copolymers using neat BlocBuilder and a protected primary amine monomer *N*-(*t*-BOC-aminopropyl)methacrylamide) (*t*BOC-MAm): a) represents the pathway to synthesize poly(styrene-*ran*-tBOC-MAm) copolymers while b) represents the pathway to synthesize poly(styrene-*ran*-methyl methacrylate-*ran*-tBOC-MAm) terpolymers.

Scheme 2. Polymerizations used to derive pendant amine functional copolymers using a protected BlocBuilder-terminated oligomer to initiate a second block containing a non-protected primary amine functional monomer, 4-aminostyrene (AST) where a) represents the route to make poly(styrene)-*block*-poly(styrene-*ran*-AST) block copolymers and b) represents the route to make poly(methyl methacrylate-*ran*-styrene)-*block*-poly(methyl methacrylate-*ran*-AST) block copoly(methyl methacrylate-*ran*-AST) block copolymers.

Fig. 1. Number average molecular weight M_n versus conversion for styrene/methyl methacrylate/N-(t-BOC-aminopropyl)methacrylamide) (ST-MMA-tBOC-MAm) terpolymerizations in 50 wt% dioxane solutions at 90 °C. Filled squares (\Box) represent the experiment ST-MMA-tBOC-MAm-10, open diamonds (\diamondsuit) represent the experiment ST-MMA-tBOC-MAm-20 and filled circles (\Box) represent the experiment ST-MMA-tBOC-MAm-20 and filled circles (\Box) represent the experiment ST-MMA-tBOC-MAm-20 and filled circles (\Box) represent the experiment ST-MMA-tBOC-MAm-20 and filled circles (\Box) represent the experiment ST-MMA-tBOC-MAm-30. The solid line represents the theoretically expected M_n versus conversion expected if the polymerization was pseudo-living.

Fig. 2. Gel permeation chromatograms (GPC) of poly(styrene-*ran*-N-(*t*-BOC-aminopropyl)methacrylamide) (ST-tBOC-MAm-20) (dashed line) and after chain extension with styrene (ST-*t*BOC-MAm-20-b-ST, solid line). Full characterization is shown in Table 4 for the macroinitiator and Table 7 for the chain-extended species.

Fig. 3. Gel permeation chromatograms (GPC) of poly(styrene-*ran*-methyl methacrylate*ran*-N-(*t*-BOC-aminopropyl)methacrylamide) (ST-MMA-tBOC-MAm-20) (dashed line) and after chain extension with a MMA/ST mixture (ST-MMA-*t*BOC-MAm-20-bMMA/ST, solid line). Full characterization is shown in Table 6 for the macroinitiator and Table 7 for the chain-extended species.

Fig. 4. Semi-logarithmic kinetic plot $\ln[(1-X)^{-1}]$ (X = monomer conversion) versus polymerization time for styrene/4-aminostyrene (ST/AST) copolymerizations initiated from benzyl amide terminated poly(styrene) (PS-BzAm, $\overline{M}_n = 3.6 \text{ kg} \cdot \text{mol}^{-1}$, $\overline{M}_w/\overline{M}_n =$ 1.13) Open circles (O) represent the copolymerization with 10 mol% AST in the feed (experiment PS-*b*-P(ST-*ran*-AST)-10) while filled squares (\blacksquare) represent the copolymerization with 30 mol% AST in the feed (experiment PS-*b*-P(ST-*ran*-AST)-30).

Fig. 5. Number average molecular weight M_n versus conversion for styrene/4aminostyrene (ST/AST) copolymerizations initiated from benzyl amide terminated poly(styrene) (PS-BzAm, $\overline{M}_n = 3.6 \text{ kg} \cdot \text{mol}^{-1}$, $\overline{M}_w/\overline{M}_n = 1.13$) Open circles (O) represent the copolymerization with 10 mol% AST in the feed (experiment PST-*b*-P(ST*ran*-AST)-10) while filled squares (\blacksquare) represent the copolymerization with 30 mol% AST in the feed (experiment PST-*b*-P(ST-*ran*-AST)-30). The solid black represents the theoretical M_n versus conversion for the copolymerizations.

Fig. 6. Gel permeation chromatograms (GPC) of a) poly(styrene)-block-poly(styreneran-4-aminostyrene) (PST-b-P(ST-ran-AST)-10) at polymerization time = 0 min and after 3 hours and b) poly(styrene)-block-poly(styrene-ran-4-aminostyrene) (PST-b-P(STran-AST)-30) at polymerization time = 0 min and after various polymerization times. Note that in b) that the polymerization was effectively halted when using a high concentration of AST in the feed.

Conditions for poly[styrene-*ran-N*-(*t*-BOC-aminopropyl)methacrylamide] P[ST-*ran-*(*t*BOC-MAm)] copolymer synthesis in 50 wt% 1,4 dioxane solution at 110 °C.

Sample Name	$f_{ m tBOC}$ -	r ^c	[<i>t</i> BOC-APMAm] ₀	$[ST]_0$	[dioxane] ₀
	Am,0 ^b		(M)	(M)	(M)
(ST-tBOC-MAm)-10	0.091	0.099	0.3	4.1	5.4
(ST-tBOC-MAm)-20	0.198	0.097	0.6	3.4	5.5
(ST-tBOC-MAm)-30	0.300	0.091	0.9	2.8	5.6

aminopropyl)methacrylamide (*t*BOC-MAm) copolymers are given as (ST-*t*BOC-MAm)xx where xx refers to the mol% of tBOC-MAm in the feed.

as

follows:

(ST)/

styrene

N-(*t*-BOC-

^bThe initial molar feed composition of *t*BOC-MAm is given by $f_{tBOC-Am,0}$.

defined

 ^{c}r is defined as the molar ratio of the initial concentration of SG1 free nitroxide to that of the BlocBuilder initiator.

Table 2

^aSample

name

is

Conditions for poly[styrene-ran-methyl methacrylate-ran-N-(t-BOC-

aminopropyl)methacrylamide] (poly[ST-ran-MMA-ran-(tBOC-MAm)]) copolymer

Sample Name ^a	$f_{\mathrm{tBOC-Am,0}^b}$	<i>f</i> мма,0 ^b	$f_{\rm ST,0}{}^b$	r ^c	[MMA] ₀ (M)	[tBOC-MAm] ₀ (M)	[ST] ₀ (M)	[dioxane] ₀ (M)
(ST-MMA- <i>t</i> BOC-MAm)- 10	0.103	0.814	0.084	0.095	3.7	0.5	0.4	5.8
(ST-MMA- <i>t</i> BOC-MAm)- 20	0.196	0.722	0.082	0.094	2.9	0.8	0.3	5.8
(ST-MMA- <i>t</i> BOC-MAm)- 30	0.298	0.614	0.088	0.101	2.2	1.1	0.3	5.9

synthesis in 50 wt% 1,4 dioxane solution at 90 °C.

^aSample name is defined as follows: styrene (ST)/methyl methacrylate (MMA)/ *N*-(*t*-BOC-aminopropyl)methacrylamide (*t*BOC-MAm) copolymers are given as (ST-MMA-*t*BOC-MAm)-xx where xx refers to the mol% of tBOC-MAm in the feed.

^bThe initial molar feed compositions of *t*BOC-MAm, MMA and ST are given by f_{tBOC-} Am,0, $f_{MMA,0}$ and $f_{ST,0}$, respectively. ^{c}r is defined as the molar ratio of the initial concentration of SG1 free nitroxide to that of the BlocBuilder initiator.

Table 3

Experimental conditions for styrene and methyl methacrylate/styrene chain extensions in 50 wt% 1,4 dioxane solution initiated from poly(styrene-*ran-N*-(*t*-BOC-

aminopropyl)methacrylamide) (poly(ST-*ran-t*BOC-MAm) and poly(styrene-*ran*-methyl methacrylate-*ran-N*-(*t*-BOC-aminopropyl)methacrylamide) (poly(ST-*ran*-MMA-*ran-t*BOC-MAm) macroinitators.

Sample ^a	[I] ^b	[ST]	[MMA]	[dioxane]
	(M)	(M)	(M)	(M)
ST-tBOC-MAm-20-b-ST	0.007	4.2	-	5.1
ST-tBOC-MAm-30-b-ST	0.007	4.0	-	4.7
(ST-MMA-tBOC-MAm)-10-b-ST/MMA	0.008	0.4	3.8	5.8
(ST-MMA-tBOC-MAm)-20-b-ST/MMA	0.009	0.4	4.0	5.7
(ST-MMA-tBOC-MAm)-30-b-ST/MMA	0.011	0.4	3.9	5.8

^aThe chain extension experiments are defined as ST-*t*BOC-MAm-xx-b-ST for the ST chain extensions from ST-*t*BOC-MAm-xx macroinitiator where xx refers to the tBOC-MAm feed composition used to make the macroinitiator. Similarly, ST-MMA-*t*BOC-MAm-xx-b-ST/MMA for the ST/MMA chain extensions from ST-MMA-tBOC-MAm-xx terpolymer macroinitiator where xx refers to the tBOC-MAm feed composition used to make the macroinitiators are provided in Table 4 and Table 5.

^b[I] is the concentration of the macroinitiator.

Characteristics of poly[styrene-*ran-N*-(*t*-BOC-aminopropyl)methacrylamide] (poly[ST*ran*-(*t*BOC-MAm)]) copolymers synthesized in 50 wt% 1,4 dioxane solution at 110 °C.

Sample Name ^a	$f_{\rm tBOC-Am,0}^{b}$	Polymerization	Xc	$\overline{M}_n^{\ d}$	$ar{M}_{w}/ar{M}_{n}{}^{ m d}$	F_{tBOC}
		time (min)		(kg·mol ⁻¹)		MAm ^e
(ST-tBOC-MAm)-10	0.091	165	0.26	9.9	1.25	0
(ST-tBOC-MAm)-20	0.20	160	0.25	11.5	1.28	0.10
(ST-tBOC-MAm)-30	0.30	165	0.35	10.9	1.34	0.14

^aSample name is defined as follows: styrene (ST)/ N-(t-BOCaminopropyl)methacrylamide (tBOC-MAm) copolymers are given as (ST-tBOC-MAm)xx where xx refers to the mol% of tBOC-MAm in the feed.

^bThe initial molar feed composition of *t*BOC-MAm is given by $f_{tBOC-Am,0}$.

 ^{c}X is the total monomer conversion by mass.

^dThe number average molecular weight \overline{M}_n and the polydispersity $\overline{M}_w/\overline{M}_n$ was determined using gel permeation chromatography (GPC) using tetrahydrofuran at 40 °C relative to linear poly(styrene) standards.

^eThe molar composition of *t*BOC-MAm in the copolymer, $F_{tBOC-MAm}$, was determined using ¹H nuclear magnetic resonance (NMR) in CDCl₃.

Characteristics of poly[styrene-*ran*-methyl methacrylate-*ran-N*-(*t*-BOCaminopropyl)methacrylamide] (poly[ST-*ran*-MMA-*ran*-(*t*BOC-MAm)]) terpolymers synthesized in 50 wt% 1,4 dioxane solution at 90 °C.

Sample Name ^a	$f_{ m tBOC}$ -	$f_{ m MMA,0}{}^b$	$\overline{\pmb{M}}_{\pmb{n}}^{\ c}$	$\overline{M}_{w}/\overline{M}_{n}^{c}$	$F_{\text{tBOC-MAm}}^d$	$F_{MMA}{}^d$
	MAm,0 ^b		(kg mol ⁻¹)			
(ST-MMA-tBOC-MAm)-10	0.103	0.814	9.7	1.49	0.08	0.82
(ST-MMA-tBOC-MAm)-20	0.196	0.722	8.2	1.51	0.09	0.80
(ST-MMA-tBOC-MAm)-30	0.298	0.614	7.9	1.57	0.21	0.68

^aSample name is defined as follows: styrene (ST)/methyl methacrylate (MMA)/ N-(t-BOC-aminopropyl)methacrylamide (tBOC-MAm) copolymers are given as (ST-MMA-tBOC-MAm)-xx where xx refers to the mol% of tBOC-MAm in the feed.

^bThe initial molar feed compositions of *t*BOC-MAm and MMA are given by $f_{tBOC-Am,0}$ and $f_{MMA,0}$, respectively.

°The number average molecular weight \overline{M}_n and the polydispersity $\overline{M}_w/\overline{M}_n$ was determined using gel permeation chromatography (GPC) using tetrahydrofuran at 40 °C relative to linear poly(styrene) standards.

^dThe molar compositions of *t*BOC-MAm and MMA in the copolymer, $F_{tBOC-MAm}$ and F_{MMA} , respectively, were determined using ¹H nuclear magnetic resonance (NMR) in CDCl₃.

Characteristics of poly(styrene-*ran-N*-(*t*-BOC-aminopropyl)methacrylamide)-*block*-poly(styrene) (poly(ST-*ran-t*BOC-MAm)-*b*-poly(ST)) and poly(styrene-*ran*-methyl methacrylate-*ran-N*-(*t*-BOC-aminopropyl)methacrylamide)-*block*-poly(styrene-ran-methyl methacrylate) (poly(ST-*ran*-MMA-*ran-t*BOC-MAm)-*b*-poly(ST-*ran*-MMA)) block copolymers

Sample ^a	$\overline{M}_n^{\mathrm{b}}$	$\overline{M}_w/\overline{M}_n^{ ext{ b}}$	F _{tBOC} -	$F_{MMA}{}^{c}$
	(kg·mol⁻¹)		MAm ^C	
ST-tBOC-MAm-20-b-ST	34.0	2.00	0.018	-
ST-tBOC-MAm-30-b-ST	37.9	1.63	0.047	-
ST-MMA- <i>t</i> BOC-MAm-10-b-ST/MMA	14.0	1.58	0.050	0.80
ST-MMA- <i>t</i> BOC-MAm-20-b-ST/MMA	12.1	1.85	0.070	0.75
ST-MMA- <i>t</i> BOC-MAm-30-b-ST/MMA	11.8	1.68	0.19	0.67

^aThe chain extension experiments are defined as ST-*t*BOC-MAm-xx-b-ST for the ST chain extensions from ST-tBOC-MAm-xx macroinitiator where xx refers to the tBOC-MAm feed composition used to make the macroinitiator. Similarly, ST-MMA-*t*BOC-MAm-xx-b-ST/MMA for the ST/MMA chain extensions from ST-MMA-tBOC-MAm-xx terpolymer macroinitiator where xx refers to the tBOC-MAm feed composition used to make the macroinitiator.

^bThe number average molecular weight \overline{M}_n and the polydispersity $\overline{M}_w/\overline{M}_n$ was determined using gel permeation chromatography (GPC) using tetrahydrofuran at 40 °C relative to linear poly(styrene) standards.

^cThe molar compositions of *t*BOC-MAm, ST and MMA in the copolymer, $F_{tBOC-MAm}$, F_{ST} and F_{MMA} , respectively, were determined using ¹H nuclear magnetic resonance (NMR) in CDCl₃.

Properties of block copolymers made by the protected initiator method: poly(styrene)-*b*-poly(styrene-*ran*-aminostyrene) (PST-*b*-P(ST-*ran*-AST)) and poly(methyl methacrylate-ran-styrene)-b-poly(methyl methacrylate-ran-aminostyrene) (P(MMA-*ran*-ST)-*b*-P(MMA-*ran*-AST)).

Expt. ID ^a	Macro	initiator	Copo	$F_{copolymer}$	
(Macroinitiator)	$ar{m{M}}_{m{n}}^{\ b}$ (kg·mol ⁻¹)	$ar{M}_{w}/ar{M}_{n}^{ ext{ b}}$	$ar{m{M}}_{m{n}}{}^{ m b}$ (kg·mol ⁻¹)	$ar{M}_{w}/ar{M}_{n}^{\ b}$	
PST-b-P(ST-ran-AST)-10	3.6	1.11	19.5	1.36	0.16 ^c
(PST-BzAm)					
PST-b-P(ST-ran-AST)-30	3.6	1.11	7.5	1.41	0.30 ^c
(PST-BzAm)					
P(MMA-ran-ST)-b-P(MMA-ran-AST)-10	6.2	1.33	16.5	1.28	0.87 ^d
(P(MMA- <i>r</i> -ST)-BzAm)					
P(MMA-ran-ST)-b-P(MMA-ran-AST)-20	6.2	1.33	15.3	1.41	0.76 ^d
(P(MMA- <i>r</i> -ST)-BzAm)					

^aThe block copolymer experiment IDs are given as follows. Poly(styrene)-*b*-poly(styrene*ran*-4-aminostyrene) block copolymers are given as PST-b-P(ST-*ran*-AST)-xx where ST = styrene, AST = 4-aminostyrene and xx refers to the mol% concentration of AST in the feed. Poly(methyl methacrylate-ran-styrene)-*b*-poly(methyl methacrylate-*ran*aminostyrene) block copolymers are given as P(MMA-*r*-ST)-b-P(MMA-*ran*-AST)-xx where MMA = methyl methacrylate, ST = styrene, AST = 4-aminostyrene and xx refers to the mol% concentration of AST in the chain extension feed.

^bThe number average molecular weight \overline{M}_n and the polydispersity $\overline{M}_w/\overline{M}_n$ were found using gel permeation chromatography (GPC) with tetrahydrofuran at 40 °C relative to linear poly(styrene) standards. Molecular weights of the PMMA-rich copolymers were estimated by using universal calibration with appropriate Mark-Houwink coefficients.

 $^{c}F_{copolymer}$ is the composition of tBOC-MAm in the copolymer determined by ¹H NMR in CDCl₃.

 $^dF_{copolymer}$ is the composition of MMA in the copolymer determined by 1H NMR in CDCl3.