

Master of Engineering Thesis

Nitroxide Mediated Synthesis of Protected Styrenesulfonate and Acrylonitrile Copolymers for Membrane and Barrier Materials

By

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Contribution of Author

The thesis is a manuscript-based thesis consisting of two manuscripts, where I, Valerie A.L. Consolante, am the first author.

The first manuscript provided in Section 2.0 is titled: "*Nitroxide Mediated Polymerization of an Organo-soluble Protected Styrenesulfonate: Development of Homo and Random Copolymers*". As a contribution to this manuscript, I have performed all the polymer syntheses, characterization, kinetic studies and interpretation of the results. I have written the manuscript, which was revised and edited by my supervisor, Dr. Milan Marić, for submission to the scientific journal "*Macromolecular Reaction Engineering*".

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The second manuscript provided in Section 3.0 is titled: "*Routes to Carboxylic Acid Functional Acrylonitrile Copolymers via Nitroxide Mediated Polymerization*". As a contribution to this manuscript, I have performed the majority of the experiments, with help from my supervisor, Dr. Milan Marić, for the styrene/acrylonitrile copolymerizations using *N*-hydroxy succinimide terminated BlocBuilder initiator. I have done all characterization, kinetic studies and interpretation of the results. I have written the first draft of the manuscript, which was revised and edited by my supervisor for submission as two separate manuscripts to the "Journal of Applied Polymer Science" (JAPS). The manuscripts are titled: 1) "*Routes to Carboxylic Acid Functional Acrylonitrile Copolymers via SG1-based Nitroxide Mediated Polymerization*" and 2) "*Testing the Versatility of a Succinimidyl-Ester Functional Alkoxyamine for Controlling Acrylonitrile Polymerizations*". Manuscript 1) has been provisionally accepted for publication (manuscript ID: APP-2011-07-2578). Manuscript 2) is currently under review (manuscript ID: APP-2011-07-2664).

Abstract

Controlled free radical polymerization is attractive as it produces polymers with well defined microstructures typically associated with "living" polymerization methods, using a wide range of monomers required for applications such as nanoporous membranes and barrier materials. Poly(trioctylammonium p-styrenesulfonate) homopolymer (poly(SS-TOA)) and poly(SS-TOA-*ran*-styrene) copolymers were synthesized by nitroxide-mediated polymerization (NMP) using an *N-tert*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide (SG1) based unimolecular initiator, called BlocBuilder. Polymerizations were controlled for low theoretical molecular weight at complete conversion ($M_{n,theoretical} = 20$ kg·mol⁻¹), resulting in very low polydispersities ($M_w/M_n < 1.1$) and a linear increase in number average molecular weight, M_n , up to $\approx 35\%$ conversion. SS-TOA was effective as a controlling co-monomer for the gradient polymerization with glycidyl methacrylate, using a *N*-succinimidyl ester modified BlocBuilder (NHS-BlocBuilder), which resulted in a relatively narrow molecular weight

distribution ($M_w/M_n = 1.43$) and linear increase in M_n versus conversion. Poly(styrene-*ran*-acrylonitrile) (poly(S/AN)) and poly(*tert*-butyl methacrylate*ran*-acrylonitrile) (poly(*t*-BMA/AN)) were also synthesized by NMP using BlocBuilder and NHS-BlocBuilder. In both systems, the polymers exhibited narrow, monomodal molecular weight distributions with relatively low polydispersities ($M_w/M_n = 1.14-1.50$), characteristic of a controlled polymerization. M_n versus conversion (X) plots were all relatively linear ($M_n =$ 14.8-18.1 kg mol⁻¹, X = 40-70%) suggesting that "pseudo-living" behaviour was approached in the range of conversions studied.

Abrégé

Cette étude se concentre sur le thème de la polymérisation radicalaire contrôlée qui est attrayante de par sa facilité à produire des polymères avec une microstructure bien définie et demeure semblable à la polymérisation ionique/vivante. Elle présente l'avantage de permettre la génération d'une vaste gamme d'application de monomères allant des membranes nanoporeuses aux matériaux barrières. Le poly(trioctylammonium p-styrènesulfonate) (poly(SS-TOA)) et poly(SS-TOA-*ran*-styrène) ont été préparés par la polymérisation contrôlée par des nitroxydes, à base de la nitroxyde *N-tert*-butyl-*N*-[1-diéthylphosphono-(2,2-diméthylpropyl)] (SG1), aussi appelé BlocBuilder. La polymérisation a été le mieux contrôlée pour un faible poids moléculaire théorique (20 kg·mol⁻¹ versus 45 kg·mol⁻¹), avec de très basses polydispersités

 $(M_w/M_n < 1.1)$ et une croissance linéaire du poids moléculaire moyen en nombre jusqu'à une conversion de $\approx 35\%$. Le SS-TOA à également prouvé son efficacité comme contrôleur comonomèrique pour la polymérisation de type gradient avec le méthacrylate glycidyl, accompagné d'une forme protégée de BlocBuilder (achevés de *N*-succinimidyl, appelé NHS-BlocBuilder). Le Poly(styrène-*ran*acrylonitrile) (poly(S/AN)) et poly(*tert*-butyl méthacrylate-*ran*-acrylonitrile) (poly(*t*-BMA/AN)) ont également été copolymérisés par polymérisation contrôlée en employant des nitroxydes avec les initiateurs BlocBuilder et NHS-BlocBuilder. Les deux systèmes ont démontré un bon degré de contrôle : une distribution de poids moléculaire étroite avec des polydispersités relativement faibles ($M_w/M_n =$ 1.14-1.50) combinée à une croissance linéaire du poids moléculaire moyen en nombre avec une conversion (*X*) relativement élevée ($M_n = 14.8-18.1 \text{ kg·mol}^{-1}, X = 40-70\%$). Ces résultats confirment bien la notion de "copolymérisation pseudovivante".

1.0 General Introduction

Block copolymers are derived from two or more covalently bonded segments which can self-assemble on macromolecular dimensions (10-25 nm) with a high potential to be used in next-generation separations membranes, surfactants^[1] and barrier materials^[2]. The covalent attachment between unlike polymeric segments in block copolymers at the molecular length scale inhibits the macrophase separation of these materials. Instead, microphase separation occurs at specific conditions, resulting in many favourable properties. Further, block copolymers are easily processed from solution and can be deposited over large areas at a low production cost, resulting in continuous efforts towards understanding and modifying these systems for nanoscale technologies.^[3]

The understanding of phase behavior governing the morphology and consequently the properties, is crucial. Flory-Huggins theory is a thermodynamic model for polymeric solutions and blends that adjusts the expression for the entropy of mixing in order to account for the dissimilarity of molecule sizes. Assuming no change in volume with mixing, only dispersive interactions and random mixing of molecules for this lattice model, Flory-Huggins theory demonstrates that in polymer blends or polymer/solvent mixtures the entropic term becomes negligible with increase in polymer chain length.^[4] The Gibbs free energy (*G*) is used to describe the system as a function of enthalpy (*H*), entropy (*S*) and temperature (*T*) as shown in *Equation 1*.

$$\Delta G = \Delta H - T \Delta S \tag{1}$$

Flory-Huggins theory reveals the following thermodynamic expression for ΔG of mixing after considering the various points above for a polymer/polymer blend:

$$\Delta G = kT \left[\frac{\phi_1}{p_1} \ln \phi_1 + \frac{\phi_2}{p_2} \ln \phi_2 + \chi_{12} \phi_1 \phi_2 \right]$$
(2)

where *k* is the Boltzmann constant, ϕ_1 and ϕ_2 are the volume fractions of polymers 1 and 2 respectively, p_1 and p_2 are the degree of polymerizations for polymers 1 and 2 respectively, and χ_{12} is the enthalpic interaction parameter to take account of the energy of the interdispersing polymer/polymer molecules. Nearly all polymers are immiscible, thus the enthalpy of mixing term ($kT\chi_2\phi_1\phi_2$) in *Equation* 2 will be positive leading to a positive Gibbs free energy of mixing and phase separation with unstable morphologies.^[5]

Block, random, or graft copolymerization is used to combine two distinctive polymer segments into a single chain. Achieving precise control of the self-assembled copolymer structure is crucial for the many applications mentioned. Thermodynamic driving forces increase the density and size uniformity of the structures compared to that obtained with conventional materials.^[6] By changing the molecular weight and relative ratio of constituent blocks, the domain size and morphology can be manipulated on the nanoscopic length scale leading to well-defined structures. These morphologies were predicted theoretically by Leibler's model^[7]. Based on the difference in polymeric segments, the enthalpically driven segregation can result in spherical, cylindrical, lamellar or gyroidal microphase morphologies as shown in Figure 1 below.^[5,7,8-9] Akin to Flory-Huggins theory, the thermodynamic stability of polymer blends and solutions can be predicted. The overall degree of polymerization (N), the volume fraction of the monomers and the enthalpic interaction parameter (χ) of the monomers involved, determine the block copolymer phase behaviour. The product of the overall degree of polymerization and the interaction parameter denotes the extent of incompatibility between blocks and likelihood to microphase separate. If $\chi N > 10.5$, microphase separation is observed for diblock copolymers of symmetric composition, while for $\chi N < 10.5$ the blocks mix without microphase separation.^[5]



Figure 1: Block copolymer microstructures for AB diblock polymeric system^[7]

Desirable microphase separated morphologies, such as those shown in Figure 1 can be obtained by careful control of the respective segments and by the choice of monomers. Further exotic morphologies and property tuning are possible when going from AB diblock to ABC triblock (i.e. shishkabob structure^[8]) copolymers. The advantage of using a triblock copolymer over a diblock copolymer is the possibility of developing and combining favourable properties of two separate diblocks (such as lateral ordering of A and high degradability of B) while eliminating undesirable properties (such as low degradability of A and no long-range order of B).^[10] Chemical etching can be used to remove the minority phase once the ordered domains are aligned.^[1,11] The use of such triblock copolymers as

precursors to highly aligned nanoporous materials is represented in Figure 2. The high surface area and spatial confinement supplied by these nanoporous materials makes them extremely useful in size selective separation. With the performance of many of these applications depending on the increase in substrate-surface interactions of the nanoporous material, the control of surface properties (charge density, functional group composition and surface energy) is critical. The ability to expand this fundamental strategy for building more sophisticated structures is a major advantage of the block copolymer route to making nanoporous materials.^[1] Thus, it is imperative to select a synthetic route that can achieve such structures while also being readily scalable for industrial manufacture.



Figure 2: Preparation of nanoporous nonoliths from triblock copolymer precursors.^[1]

Free-radical polymerization (RP) is an important commercial process to produce high molecular weight polymers. It can be done under mild reaction conditions that are fairly oxygen tolerant and water tolerant.^[12] The drawback to RP is the inability to control molecular weight, polydispersity, composition and functionality; these are all essential when trying to obtain block copolymers with controlled microstructure. Ionic or "living" polymerization allows for welldefined polymers; however, it requires the protection of functional groups and rigorous reagent purification. It is thus desirable to attain precise control of microstructure while being easily implemented industrially like RP processes. Controlled radical polymerization (CRP) allows for controlled microstructure and molecular weight, which was previously only possible by ionic "living" polymerizations. CRP has the ability to adapt RP technologies to produce welldefined polymers. Unlike living polymerizations, CRP can make controlledmicrostructure resins in aqueous systems: solution, emulsion, mini-emulsion.^[13-15] In all cases, it allows for the simultaneous growth of all chains by reversible exchange between dormant and active species (reversible termination or chain transfer), resulting in a sufficiently low kept radical concentration. The latter allows for minimal irreversible termination during a large portion of the polymerization.^[16,17]

The three most common techniques for CRP include nitroxide mediated polymerization (NMP),^[18-23] atom transfer radical polymerization (ATRP)^[24,25] and reversible addition fragmentation transfer polymerization (RAFT)^[26,27]. There are advantages and disadvantages to each technique that can be compared based on reaction conditions, nature of transferred end groups, additives or catalysts and the range of polymerizable monomers. ATRP relies on a catalyst/ligand system which must be removed or recycled and RAFT relies on a radical source (initiator) and a chain transfer agent (CTA) to provide control and to ensure chain

end functionality. Further additives are not needed for NMP, except in the special case where rate acceleration is necessary.^[16] NMP based on TEMPO (2,2,6,6tetramethylpiperidine-N-oxyl), a first generation nitroxide, was effective for the polymerization of styrenic monomers.^[28-30] Advances in the design of nitroxide based initiators have extended the range of monomers polymerizable by NMP. In the early 2000s, controlled poly(n-butyl acrylate)^[31] and poly(acrylic acid)^[32] were synthesized by NMP using *N-tert*-butyl-*N*-[1-diethylphosphono-(2,2dimethylpropyl)] nitroxide (SG1) (Figure 3) and an SG1-based initiator called MONAMS. The ability of such alkoxyamine-based initiators to control acrylate polymerizations makes them more versatile than TEMPO, as lower temperatures can be used (< 100°C compared to 120°C required with TEMPO).^[32,33] More nitroxides^[34] effective second-generation like N-(2-methylpropyl)-N-(1diethylphosphono-2,2-dimethylpropyl)-O-(2-carboxylprop-2-yl) hydroxylamine (BlocBuilder, commercially available from Arkema, Inc.) and 2,2,5-trimethyl-4phenyl-3-azahexane nitroxide (TIPNO) have been able to control homopolymerizations of acrylates, acrylamides and methacrylates. In the latter case, using a controlling co-monomer like styrene at a low concentration (~ 5 mol%) ensures good control of the polymerization and subsequent ability to form block copolymers.^[35] More recent work has reported controlled methacrylate homopolymerizations using nitroxides formed *in situ* from nitrites, 2,2-diphenyl-3-phenylimino-2,3-dihydroindol-1-yloxyl nitroxide (DPAIO), and Nphenylalkoxyamines.^[22,36-39]



Figure 3: Structures of initiators: a) TEMPO, b) SG1 (free nitroxide) and c) BlocBuilder (unimolecular initiator).

In some cases, CRP has permitted the incorporation of functional groups not possible with living polymerizations,^[40] such as the sulfonate group, of interest for nanoporous separations media, fuel cells, catalysis, reverse osmosis water desalination and biomineralization applications.^[15,40,41] Thus, the first study in this thesis focused on testing the amenability of NMP to polymerize an organosoluble protected sulfonate monomer, trioctylammonium p-styrenesulfonate (SS-TOA), and then to statistically copolymerize SS-TOA/styrene feeds using BlocBuilder. The results of this study, for example, will be useful for developing NMP methods to produce block/gradient^[42] copolymers suitable for nextgeneration nanoporous separations membranes with sulfonate groups on the membrane walls^[1].

Additionally, CRP has allowed the incorporation of acrylonitrile into styrenic resins, which is appealing for barrier applications against organic liquids and gases, such as for fuel tanks, packaging of food and pharmaceutical products. CRP can be used to achieve the desirable placement of functional groups

necessary in polymers to compatibilize polymer blends through the formation of block copolymers by melt-coupling. Careful manipulation of the melt-blending process via reactive blending enables the formation of morphologies needed for barrier applications.^[43] For example, nylon is compounded into a polyethylene matrix as a dispersed laminar phase acting as a barrier to prevent the polyolefin from swelling.^[44] The morphologies are stabilized by reactive blending between the amino groups in the nylon and functional groups, such as maleic anhydride, grafted onto the polyolefin.^[45] More attractive is to include functional groups that are not a residue of the original polymerization process (such as in the case for nylon), in order to produce a wider range of barrier materials for several applications. The second study in this thesis thus examined a unique approach to develop new barrier polymers based on poly(styrene-ran-acrylonitrile) (poly(S/AN)) with functional groups either on the chain end or along the chain using NMP. These would be subsequently reacted with a suitably functionalized commercial polyolefin in an extruder to produce desirable, stable blend morphology. The AN co- and terpolymers resulting from this study could be used as an initial phase for future sophisticated designs of AN-containing resins desirable for barrier applications.

2.0 Nitroxide Mediated Polymerization of an Organo-soluble Protected Styrenesulfonate: Development of Homo and Random Copolymers

Abstract

A protected styrenesulfonated monomer, trioctylammonium p-styrenesulfonate (SS-TOA), was polymerized at 90°C-105°C by nitroxide mediated polymerization (NMP) using N-(2-methylpropyl)-N-(1-diethylphosphono-2,2-dimethylpropyl)-O-(2-carboxylprop-2-yl) hydroxylamine (BlocBuilder) unimolecular initiator and additional additional *N-tert*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)] free nitroxide (SG1). Polymerizations were controlled for low theoretical molecular weight $(M_{n,\text{theoretical}} = 20 \text{ kg} \cdot \text{mol}^{-1})$, resulting in very low polydispersities $M_{\rm w}/M_{\rm n} < 1.1$) and a linear increase in number average molecular weight, $M_{\rm n}$, up to \approx 35% conversion. Product of the propagation rate constant k_p and equilibrium constant K $(k_p K)$ for SS-TOA was 1.5-2 times greater than styrene at the same temperature, suggesting it may be suitable as a controlling co-monomer for BlocBuilder mediated NMP with methacrylates. SS-TOA was effective as a controlling co-monomer for a gradient polymerization with glycidyl methacrylate, using a N-succinimidyl ester modified BlocBuilder. The resulting copolymer possessed a relatively narrow, monomodal molecular weight distribution (M_w/M_n) = 1.43) and a linear increase in M_n with conversion, suggesting the suitability of SS-TOA as a useful NMP co-monomer.

2.1 Manuscript Introduction

Controlled radical polymerization (CRP)^[12] has enabled polymer chemists to approach the control of microstructure and molecular weight distribution, hallmarks of truly "living" polymerizations, with a relaxation of the conditions required of the latter (air-free transfers, functional group protection, rigorously pure reagent purification). CRP has achieved this control by various methods, such as those employing a reversible chain transfer (eg. RAFT)^[26,27,46] or a reversible termination process (eg. nitroxide mediated polymerization (NMP)^{[18,20-^{23]} or atom transfer radical polymerization (ATRP)^[24,25]). The ability to make controlled structures, like those such as amphiphilic block copolymers, has been targeted and achieved by CRP.^[15,47-55] In some cases, CRP has permitted the combination of two monomer types or incorporation of functional groups that were not possible with living polymerizations.^[40]}

One such functional group is the sulfonate group, which is of interest for nanoporous separations media, fuel cells, catalysis, reverse osmosis water desalination and biomineralization^[15,40,41] The direct sequential polymerization of block copolymers containing sulfonate groups in one segment is difficult for two reasons. First is the incompatibility of sulfonate monomers with controlled polymerization due to the highly charged and acidic species, which can degrade an initiator such as that used for NMP or poison a catalyst such as that used by ATRP. However, neutralization can be done and is easy to do in aqueous media.^[56-59] Second is the strong immiscibility of the hydrophilic sodium p-

styrenesulfonate (SS-Na) and poly(styrenesulfonic acid, sodium salt) (poly(SS-Na)) with hydrophobic monomers and organic solvents (i.e. homogenous solutions). This is the case even if the hydrophilic homopolymer block is synthesized in a controlled manner. To overcome these difficulties, postmodification of the precursor polymer or protection chemistry prior to synthesis is necessary, even when employing a CRP technique. Block copolymers containing poly(styrenesulfonate) segments have been made by selective post-polymerization sulfonation of poly(styrene), although there are several disadvantages to this technique. There is a possibility of side reactions that lead to intramolecular sulfone linkages, as it is not always possible to selectively sulfonate the poly(styrene) block and it is difficult to reach 100% sulfonation of the poly(styrene) block.^[60,61] An alternative method involves modifying the pstyrenesulfonate monomer to a more hydrophobic form that is compatible with the desired polymerization chemistry. Using such an approach, Okamura and coworkers converted the sulfonic acid group to a sulfonate ester, which can be hydrolyzed back to the acid form after polymerization^[62]. A third method is to neutralize the sulfonic acid site on the monomer with trioctylamine to produce a hydrophobic trioctylammonium p-styrenesulfonate monomer^[40,63,64], as shown in Figure 4a. This avoids having to use light sensitive silver sulfonate salts or water sensitive sulforvl chlorides as in the second method, where a sulfonate ester is prepared. The acid-base neutralization with trioctylamine has been used by Cavicchi and co-workers to prepare different ionic liquid polymers using RAFT by altering the tertiary amine and the chemistry of the acidic monomer.^[40] It is a simpler and cheaper approach than the previous two methods and has been employed for the purpose of these works.

The controlled radical polymerization of trioctylammonium pstyrenesulfonate (SS-TOA) monomers has been demonstrated by using reversible addition fragmentation transfer polymerization (RAFT)^[40]. Nitroxide mediated polymerization (NMP)^[65] is desirable due to its simplicity, particularly when using unimolecular initiators such as N-(2-methylpropyl)-N-(1-diethylphosphono-2,2-dimethylpropyl)-*O*-(2-carboxylprop-2-yl) hydroxylamine (BlocBuilder, commercially available from Arkema. Inc.)^[34]. Thus, the following study focused on testing the amenability of NMP to polymerize SS-TOA and then to statistically copolymerize SS-TOA/styrene feeds using BlocBuilder. The latter is also here studied; as statistical copolymers are a step towards making gradient or tapered copolymers that could approximate the microphase separated microstructures associated with block copolymers. Gradient copolymers are attractive from an industrial perspective since an intermediate purification and re-initiation step is avoided.

A more attractive use of SS-TOA in copolymerization would be to use it not only to impart the desirable sulfonate functionality, but also as a controlling co-monomer for the BlocBuilder-controlled polymerization of methacrylates. Traditionally, NMP was limited to styrenic monomers using first-generation nitroxides such as 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO) but secondgeneration nitroxides like BlocBuilder and 2,2,5-trimethyl-4-phenyl-3-azahexane nitroxide (TIPNO) have been able to control homopolymerizations of acrylates, acrylamides and nearly pure methacrylates, provided that a low concentration ~ 5 mol% controlling co-monomer like styrene was used for the latter.^[35] More recent work has shown that methacrylate homopolymerizations could be controlled using the nitroxides such as those formed *in situ* from nitrites, 2,2-diphenyl-3-phenylimino-2,3-dihydroindol-1-yloxyl nitroxide (DPAIO), and *N*-phenylalkoxyamines.^[22,36-39]

The functionality of the SS-TOA monomer and its potential to control methacrylates by NMP coincides well for application to nanoporous membranes templated from block or gradient copolymers. For ABC triblock copolymers desired for nanoporous templates (A = sacrificial segment, B = functional segment, C = tough, matrix segment), the SS-TOA units could serve as the precursor for sulfonic acid sites on a membrane wall while the poly(methacrylate)^[66] could serve as the matrix material. Even more desirable is to use a methacrylate that could be cross-linked, like the epoxy-functional glycidyl methacrylate (GMA)^[67], which we have recently shown to be controllable with styrene co-monomer using *N*-succinimidyl terminated BlocBuilder (NHS-BlocBuilder)^[68]. We thus attempt to also determine if an SS-TOA/GMA gradient^[48] copolymerization could be controlled by NMP with NHS-BlocBuilder. The NHS group from the initiator fragment could later be transformed into an initiator for lactone or lactide polymerizations to provide the

selectively degradable segment required of nanoporous membranes. The results of this study, for example, will be useful for developing NMP methods to produce block/gradient^[42] copolymers suitable for next-generation nanoporous separations membranes with sulfonate groups on the membrane walls^[1].

2.2 Experimental Section

2.2.1 Materials

Trioctylamine (TOA) (99%), 4-styrenesulfonic acid - sodium salt, basic alumina (Brockmann, Type 1, 150 mesh), calcium hydride (90-95%, reagent grade) were obtained from Sigma-Aldrich and used as received. Hexane (98.5%), cyclohexane tetrahydrofuran (99.9%), toluene (99.8%), (99.5%). benzene (99.8%), hydrochloric acid (37 wt% solution) were obtained from Fisher and used as received. Deuterated chloroform (CDCl₃) was obtained from Cambridge Isotope Laboratories. N-(2-methylpropyl)-N-(1-diethylphosphono-2,2-dimethylpropyl)-O-(2-carboxylprop-2-yl) hydroxylamine (BlocBuilder[®]) (99%) was obtained from Arkema and N-*tert*-butyl-N-[1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide) (SG1) (85%) was kindly donated by Noah Macy of Arkema and used as received. *N*-hydroxysuccinimide (98%) and N,N'-dicyclohexylcarbodimide (DCC, 99%) were received from Sigma-Aldrich and used in conjunction with BlocBuilder to synthesize the succinimidyl ester terminated alkoxyamine BlocBuilder (NHS-BlocBuilder) using the same procedure as Vinas et al.^[68] Styrene (99%) and glycidyl methacrylate (GMA, 97%) purchased from Sigma-Aldrich, were purified by passing through a column of basic alumina mixed with 5% calcium hydride, then sealed with a head of nitrogen and stored in refrigeration until needed.

2.2.2 Synthesis of Trioctylammonium p-Styrenesulfonate Monomer

Trioctylammonium p-styrenesulfonate (SS-TOA) was synthesized from the two step procedure described by Liu et al^[40,69]. In the first step, TOA was dissolved in hexane and HCl was added drop-wise (in an ice bath). The solution was placed in a freezer overnight to form trioctylammonium hydrochloride, that was then filtered, washed with cold hexane (to remove excess HCl) and dried under vacuum to form a white precipitate, trioctylammonium hydrochloride (TOA-HCl). In the second step, two solutions: TOA-HCl dissolved in benzene and sodium p-styrenesulfonate dissolved in deionized water, were combined, mixed and left to settle several hours in a separation funnel. The organic layer was collected and concentrated, frozen, filtered and then dried under vacuum overnight to yield the white SS-TOA product shown in Figure 4a; yield 21.3 g (90.7%). ¹H NMR: δ 10.4 (1H, SO₃H) 7.84 (2H, aromatic), 7.42 (2H, aromatic), 6.70 (1H, CH₂=CH–), 5.81(H, CH₂=CH–), 5.31(H, CH₂=CH–), 3.02 (6H, N– CH₂–), 1.71 (6H, N–CH₂–CH₂–), 1.27 (30H, –CH₂–), 0.89 (9H, CH₃).







Figure 4: Synthesis of (a) Trioctylammonium p-styrenesulfonate (SS-TOA) Monomer (b) trioctylammonium p-styrenesulfonate Homopolymers (poly(SS-TOA)) and (c) Trioctylammonium p-styrenesulfonate/Styrene random Copolymers (poly(SS-TOA-*ran*-S)).

(a)

2.2.3 Synthesis of Trioctylammonium p-Styrenesulfonate Homopolymers (poly(SS-TOA))

Nitroxide mediated homopolymerization experiments of SS-TOA (Figure 4b) in toluene were conducted at various temperatures: 90°C, 95°C, 100°C and 105°C. All homopolymerizations were performed in a 100 mL three-neck round bottom glass flask equipped with a magnetic stir bar, condenser and thermal well. The flask was set inside a heating mantle and placed on a magnetic stirrer. SS-TOA monomer and toluene (20 to 25 wt % solutions) were added to the flask with the stirrer according to the experimental conditions and formulations presented in Table 1. Two theoretical molecular weights at complete conversion were studied: 20 kg·mol-1 and 45 kg·mol-1, calculated by the mass of monomer relative to the moles of BlocBuilder initiator. As an example, for experiment ID SS-TOA-100, BlocBuilder (0.031 g, 0.081 mmol) and SG1 free nitroxide (0.0020 g, 0.0068 mmol, 8.5 mol% relative to BlocBuilder) were added to the flask, which was then sealed with a rubber septum. The central neck was connected to a condenser and capped with a rubber septum with a needle to relieve pressure applied by the nitrogen purge throughout the reaction. A thermocouple was connected to a controller and inserted into the third neck of the flask. As stirring began and SS-TOA monomer was dissolved, the chilling unit (Neslab 740) using a glycol/water mixture that is connected to the condenser was set to 5°C. A nitrogen flow was introduced to purge the solution for 30 minutes. The reactor was heated to 100°C at a rate of about 5°C·min-1 while maintaining the purge. Once the reaction reached the set-point temperature, the first sample was taken (t = 0, start of the reaction) with a 1 mL syringe followed by periodic sampling until the solution became too viscous to withdraw from. A portion of the sample was placed in a 5 mm Up tube for nuclear magnetic resonance (NMR) analysis. The remaining sample was precipitated in hexane, left to settle for several hours, then decanted and dried overnight in a vacuum oven at 60°C. In particular, for the synthesis using 1.60 g SS-TOA with target average molecular weight at complete conversion of 20 kg·mol⁻¹ at 100°C (SS-TOA-100), the final yield after 180 minutes was 0.85 g (52% conversion based on gravimetry) with number-average molecular weight $M_n = 13.2$ kg·mol⁻¹, weight average molecular weight $M_w = 16.9$ kg·mol⁻¹ and polydispersity index of $M_w/M_n = 1.28$ determined by gel permeation chromatography calibrated with linear poly(styrene) standards in TOA/THF at 40°C. The conversion was 51% based on ¹H NMR in CDCl₃.

2.2.4 Synthesis of Trioctylammonium p-Styrenesulfonate/Styrene Random Copolymers (poly(SS-TOA-ran-S))

The SS-TOA/S copolymerization (Figure 4c) experiments were performed in a 25 mL three neck-round bottom glass flask equipped with a magnetic stir bar, condenser and thermal well. The flask was set inside a heating mantle and placed on a magnetic stirrer. Formulations for initial molar feed compositions, $f_{\text{SS-TOA},0} = 0.10-0.80$ were followed. Target molecular weights, calculated based on the mass of SS-TOA and styrene monomers relative to BlocBuilder initiator (0.031 g,

0.081 mmol), were nearly 30 kg·mol-1 for all experiments. 8.4 mol% SG1 free nitroxide relative to BlocBuilder was used to help control the polymerization. SS-TOA monomer and toluene (35 and 45 wt % solutions) were added to the flask with the stirrer according to the formulations for the set of SS-TOA/S copolymerizations presented in Table 2. BlocBuilder and SG1 free nitroxide were added to the flask, which was then sealed with a rubber septum. The central neck was connected to a condenser and capped with a rubber septum with a needle to relieve pressure applied by the nitrogen purge throughout the reaction. A thermocouple was connected to a controller and inserted into the third neck of the flask. As stirring began and the SS-TOA monomer was dissolved, the chilling unit (Neslab 740) using a glycol/water mixture that is connected to the condenser was set to 5°C to reflux any vapors produced during the experiments in order to prevent the loss of any styrene monomer due to evaporation (SS-TOA monomer is non-volatile). The previously purified styrene monomer was then injected into the flask using a disposable 5 mL syringe to accurately obtain the required feed compositions. A nitrogen flow was introduced to purge the solution for 15 minutes. The reactor was heated to 110°C at a rate of about 5°C·min⁻¹ while maintaining the purge. The time when the reaction reached the set-point temperature was taken as the start of the reaction (t = 0). The first sample was taken after a 15 minute reaction time with a 1 mL syringe followed by periodic sampling over 2 to 3 hours. This was done to determine reactivity ratios, as low conversions are necessary to avoid any corrections for compositional drift. The

samples were precipitated in hexane, left to settle for several hours, then decanted and dried overnight in a vacuum oven at 60°C. A portion of the dried sampled was taken and inserted in 5 mm Up tubes for determining the compositions using NMR. In particular, for an initial feed composition of SS-TOA equal to 40 mol% $(f_{SS-TOA,0} = 0.4, 1.90 \text{ g SS-TOA} \text{ and } 0.57 \text{ g styrene})$ with target average molecular weight of 30 kg·mol⁻¹ at 110°C, the final yield after 120 minutes was 1.68 g with a composition of 45 mol% SS-TOA in the copolymer using NMR spectroscopy. To establish the reactivity ratios of SS-TOA and styrene, the number average molecular weight $M_n = 3.0 \text{ kg·mol}^{-1}$, weight average molecular weight $M_w = 3.2 \text{ kg·mol}^{-1}$ and polydispersity index of $M_w/M_n = 1.06$ were determined by gel permeation chromatography calibrated with linear poly(styrene) standards in TOA/THF at 40°C.

2.2.5 Synthesis of Trioctylammonium p-Styrenesulfonate/Glycidyl Methacrylate Gradient Copolymer (poly(SS-TOA-grad-GMA))

A gradient copolymerization experiment of SS-TOA with GMA in toluene was conducted at 90°C. A similar procedure used for the SS-TOA polymerizations and SS-TOA/styrene copolymerizations described in detail above was followed. 0.5 g of SS-TOA was used, with a *N*-succinimidyl terminated BlocBuilder (NHS-BlocBuilder, 0.028 g, 0.063 mmol), in toluene (10 wt% of monomer in solvent). NHS-BlocBuilder is an attractive molecule as it is convenient for the functionalization of polymer chain ends. It has been an efficient initiator for styrene and *n*-butyl acrylate polymerizations.^[68] We expect that the NHS can serve as a protecting group, but also it should sufficiently release enough SG1 from the start of the reaction to effectively control methacrylic polymerizations, such as for GMA. We seek to determine whether NHS-BlocBuilder would be an effective controller for SS-TOA/GMA gradient copolymerization without any added free nitroxide. After 220 min of reaction, 5.0 g of GMA was injected into the reactor and left to polymerize further for 3 hours. A portion of the sample was placed in 5 mm Up tube for nuclear magnetic resonance (NMR) analysis immediately before injecting GMA and during the following three hours of polymerization. During sampling, another portion was precipitated in hexane, left to settle and dried overnight in a vacuum oven at 60°C for molecular weight analysis in the GPC.

2.2.6 Characterization

¹H NMR spectra were measured using a 300 MHz and 400 MHz Varian Gemini 2000 spectrometer. Samples were dissolved in deuterated chloroform at a concentration of 10 mg/mL in 5 mm Up NMR tubes and were scanned 32 times. The molecular weight and molecular weight distribution of the homopolymers and copolymers were characterized by gel permeation chromatography (GPC) using a Waters Breeze system equipped with three Styragel columns (molecular weight ranges: HR1: $10^2 - 5 \times 10^3$ g·mol⁻¹, HR2: $5 \times 10^2 - 2 \times 10^4$ g·mol⁻¹, HR3: 5×10^3 - 6×10^5 g·mol⁻¹) and a guard column heated to 40°C during analysis. Tetrahydrofuran (THF) was initially used as the mobile phase with an applied flow rate of 0.3 mL·min⁻¹ during analysis. Non-polar polymers containing a low quantity of polar units can have unusual solution properties.^[70-73] Polar polymers, like poly(SS-TOA), tend to have smaller hydrodynamic volumes in the THF solvent compared to poly(styrene) and tend to adsorb onto the column. Since a solvent's properties can be reproduced with a mixture of solvents, an appropriate solvent system should be possible to diminish the adsorption properties or solvation effects of polymers with polar and non-polar properties. For example, polar polymers with sulfonate groups as ionic substituents have a reduced solubility in non-polar solvents and a two-component solvent system of 2 wt% TOA in THF was required and used to fully dissolve the polymer.^[74] The GPC was also equipped with ultraviolet (UV 2487) and differential refractive index (RI 2410) detectors. The molecular weights were reported relative to calibration with linear, narrow molecular weight distribution poly(styrene) standards.

2.3 **Results and Discussion**

2.3.1 Trioctylammonium p-Styrenesulfonate Homopolymers (poly(SS-TOA))

The prepared SS-TOA monomer was soluble in several solvents including toluene, benzene, chloroform, tetrahydrofuran, methanol, and cyclohexane at room temperature. The ¹H NMR spectrum of the monomer confirmed a stoichiometric amount of trioctylamine to styrene sulfonic acid as reported by Liu et al.^[40] SS-TOA was polymerized by NMP in 20 to 25 wt% solutions in toluene at 90°C, 95°C, 100°C, 105°C with 8.5 mol% SG1 free nitroxide relative to

BlocBuilder initiator (Table 1). Samples were taken during the polymerizations to monitor the conversion throughout the reaction. The conversion was determined by comparing the ¹H NMR peak at 3.02 ppm of the methyl groups in trioctylamine, present in both the monomer and polymer, to the peaks at 5.3 and 5.8 ppm corresponding to the vinyl peaks present only in the monomer. Figure 5 shows the first-order kinetic plot of $ln(1-X)^{-1}$ versus time for SS-TOA polymerizations at various temperatures. Conversion increased in a linear fashion for all four experiments, implying a constant radical concentration in the conversion ranges studied.



Figure 5: Semilogarithmic plot of $ln(1-X)^{-1}$ (where X = conversion) versus time for homopolymerizations of trioctylammonium p-styrenesulfonate (SS-TOA) at various temperatures for two target molecular weights using 8.5 mol% SG1 free nitroxide relative to BlocBuilder. The various temperatures are represented symbolically by: (\bullet) 90°C, (\diamondsuit) 95°C, (\blacksquare) 100°C, (\bigtriangleup) 105°C. Filled symbols

denote M_n versus X for homopolymerizations with a target molecular weight of 20 kg·mol⁻¹ (-----), while open symbols denote M_n versus X for homopolymerizations with a target molecular weight of 45 kg·mol⁻¹ (- - - -). Note the plots do not always pass 0. The time for the start of the reaction was taken once the desired temperature was reached, but polymer may have formed as a high temperature (> 80°C) was approached.

The first-order kinetic plot shown in Figure 5 was used to estimate the kinetic parameters for the SS-TOA polymerizations at various temperatures. The slopes are equal to $\langle k_p \rangle [P \cdot]$ where $\langle k_p \rangle$ is the propagation rate constant and [P] is the concentration of propagating macro-radicals. In each experiment, more kinetic information can be obtained given the expression for the equilibrium between dormant and active chains. *Equation 3* gives the equilibrium constant, $\langle K \rangle$, which is defined as:

$$\left\langle K \right\rangle = \frac{[P \cdot][SG1]}{[P - SG1]} \tag{3}$$

where [P'] is the concentration of propagating macro-radicals, [SG1] is the concentration of free nitroxide, and [P-SG1] is the concentration of SG1-capped species. Multiplying *Equation 3* by the propagation rate constant, $\langle k_p \rangle$, gives the following expression.

$$\langle k_p \rangle \langle K \rangle = \langle k_p \rangle \frac{[P \cdot][SG1]}{[P - SG1]}$$
(4)

Since the initial concentration of free nitroxide $[SG1]_0$ is high, [SG1] will not vary much and thus $[SG1] \approx [SG1]_0$. If the polymerization is assumed to be "pseudoliving", then [P-SG1] can be substituted by the initial concentration of BlocBuilder initiator ([BlocBuilder]_0) resulting in *Equation 5*.

$$\langle k_p \rangle \langle K \rangle \approx = \langle k \rangle_p \frac{[P \cdot][SG1]_0}{[BlocBuilder]_0}$$
(5)

These assumptions should be satisfactory since M_n versus conversion is linear in the studied range as shown in Figure 5, thus *Equation 5* can be rewritten as *Equation 6 to* estimate the kinetic parameters.

$$\langle k_p \rangle \langle K \rangle \approx = \langle k_p \rangle [P \cdot] r$$
 (6)

The parameter $r = [SG1]_0/[BlocBuilder]_0$ in Equation 6 is defined as the initial molar ratio of free nitroxide to that of BlocBuilder initiator. For this work, representative rate/equilibrium constant values, $\langle k_p \rangle \langle K \rangle$, were determined from experiments with an *r-value* of 0.085 and are presented in Table 3 as a function of temperature. The $\langle k_p \rangle \langle K \rangle$ values for SS-TOA polymerizations can be compared to styrene $\langle k_p \rangle \langle K \rangle$ values that have been previously reported by various research groups.^[21,37,75-78] The $\langle k_p \rangle \langle K \rangle$ values for SS-TOA are greater than for styrene by a factor of ~1.4-2. However, as temperature increased the SS-TOA polymerizations approached the styrene polymerization kinetic parameters more closely.

Poly(SS-TOA) seemed soluble in THF, but a very weak detector response was observed from the refractive index detector during GPC measurements using THF as the eluting solvent. The sulfonate groups (ionic substituents) in the homopolymer are not fully soluble in THF, resulting in column interactions and thus some tailing is apparent in the GPC traces. Due to this phenomenon, the resulting M_n values from the chromatogram are larger than expected. Adding trioctylamine (TOA) to THF (2 g TOA/100 mL THF) has been found to completely dissolve the SS-TOA homopolymers and reduces the strong interactions to the column, thus improving the intensity from the refractive index detector.^[40] The M_n versus conversion plots approached the theoretical values for poly(styrene) standards more closely when using the 2wt% TOA in THF solvent system as opposed to using only THF as solvent. This result is shown in Figure 6 for SS-TOA-100 with target molecular weight of 20 kg·mol⁻¹ conducted at 100°C.



Figure 6: Trioctylammonium p-styrenesulfonate homopolymerization (SS-TOA-100) at 100°C with target molecular weight of 20 kg·mol⁻¹ using 8.5 mol% SG1 free nitroxide relative to BlocBuilder

The conversions and molecular weight characteristics of the SS-TOA homopolymers are summarized and presented in Table 5. From Figure 7 a linear increase in M_n with conversion was observed for SS-TOA-90 and SS-TOA-100, (the experiments with a lower theoretical molecular weight at complete conversion of 20 kg·mol⁻¹) until about 35 % conversion. For SS-TOA-95 and SS-TOA-105, (the experiments with a lower theoretical molecular weight at complete conversion of 45 kg·mol⁻¹) the molecular weights initially overshoot the theoretical values and flatten as conversion increases. In all cases, the molecular weights obtained from the poly(styrene) standards deviated from the estimated theoretical linear behavior anticipated for a controlled polymerization. This is expected, as the elution time is proportional to the hydrodynamic radius of the

polymer^[79] which may be different for poly(SS-TOA) compared to poly(styrene), either in THF or in the solvent system of 2 wt% TOA in THF. It is more difficult to control the high target molecular weight polymers, due in part to the increase in solution viscosity with increase in polymer $M_{\rm n}$.^[80] This can be seen in Figure 7 for SS-TOA-95 and SS-TOA-105, where M_n values do not increase linearly above 10% conversion but level off or even decrease at higher conversion. With the polymerizations targeting a higher theoretical molecular weight, there is more monomer present relative to initiator and polymer and thus it is likely that chain transfer and related side reactions will be more prevalent. Increasing the SG1 to BlocBuilder molar ratio may aid with the control of these polymerization experiments.^[76] Still, polymerization experiments SS-TOA-90 and SS-TOA-100 with target molecular weights of 20 kg·mol⁻¹ were more controlled as compared to SS-TOA-95 and SS-TOA-105 with target molecular weights of 45 kg·mol⁻¹, giving polymers with polydispersity indices, M_w/M_n , as low as 1.02 and a linear increase in number average molecular weight, M_n , with conversion up to about 35%. This range is satisfactory, as many applications may not require high degrees of polymerization of the SS-TOA.


Figure 7: Number-average molecular weight (M_n) versus conversion (X) for trioctylammonium p-styrenesulfonate homopolymerizations at various temperatures for two target molecular weights using 8.5 mol% SG1 free nitroxide relative to BlocBuilder. The various temperatures are represented symbolically by: (•) 90°C, (\diamond) 95°C, (\blacksquare) 100°C, (\triangle) 105°C. Filled symbols denote M_n versus X for homopolymerizations with a target molecular weight of 20 kg·mol⁻¹ (---), while open symbols denote M_n versus X for homopolymerizations with a target molecular weight of 45 kg·mol⁻¹ (---).

At the lower target molecular weight experiments (20 kg·mol⁻¹), the polydispersities tend to increase relatively linearly, while at the higher target molecular weight experiments (45 kg·mol⁻¹), the polydispersities show a different trend. For SS-TOA-105, M_w/M_n values decrease from 1.35 to 1.18 until 15% conversion and then increase from 1.10 to 1.18 between 15% to 30% conversion. Similarly for SS-TOA-95, M_w/M_n values decrease from 1.18 to 1.11 until 15% conversion and then increase from 1.11 to 1.20 up to 30% conversion. The latter

are typical in M_w/M_n trends, as at early conversions the polymerization was less controlled but leveled at later conversions showing better control, despite the downward deviation in M_n from $M_{n,\text{theoretical}}$ which indicates an increase in the rate of chain transfer is likely. The slight increase in M_w/M_n towards the end of the reaction may suggest irreversible chain transfer reactions to the solvent or consecutive side reactions onto intermediate radicals.^[81] Trialkylamines have been observed to act as chain transfer agents where hydrogen abstraction from the α carbon of the trialkylamine produces a new initiating radical.^[82] Consequently, lowering the target molecular weight induces an improvement in the control of the polymerization.



Figure Polydispersity $(M_{\rm w}/M_{\rm n})$ 8: index versus conversion (X)for trioctylammonium p-styrenesulfonate homopolymerizations at various temperatures for two target molecular weights using 8.5 mol% SG1 free nitroxide relative to BlocBuilder. The various temperatures are represented symbolically

by: (•) 90°C, (\diamond) 95°C, (\blacksquare) 100°C, (\triangle) 105°C. Filled symbols denote M_w/M_n versus X for homopolymerizations with a target molecular weight of 20 kg·mol⁻¹ (---), while open symbols denote M_w/M_n versus X for homopolymerizations with a target molecular weight of 45 kg·mol⁻¹ (---).

2.3.2 Trioctylammonium p-Styrenesulfonate/Styrene Random Copolymer (poly(SS-TOA-ran-S))

The SS-TOA-*ran*-S copolymerizations done in toluene at 110°C, with target molecular weights of 30 kg·mol⁻¹ and with molar feed compositions, $f_{SS-TOA,0}$, ranging from 0.10 to 0.80, are summarized in Table 5. Copolymerization is desirable as it may not be necessary to have the functional SS-TOA units as a homopolymer segment in all applications. Copolymer compositions were determined by NMR spectroscopy at less than 10 mol% conversion such that no significant compositional drift would be expected.^[83] The GPC traces for several copolymerizations are displayed in Figure 9a-d using the solvent system of 2 wt% TOA to THF, again to prevent the strong interactions of the sulfonate groups to the GPC columns. The traces were monomodal in nature, with low polydispersities ($M_w/M_n < 1.3$) characteristic of a controlled polymerization.



Figure 9: Gel permeation chromatograms of samples taken at various times for SS-TOA/S copolymerizations poly(SS-TOA-*ran*-S) performed at 110°C in toluene with theoretical molecular weights at complete conversion of 30 kg·mol⁻¹ and with different monomer feed concentrations (initial molar feed concentration of SS-TOA is given by $f_{SS-TOA,0}$) using SG1/BlocBuilder initiator: (a) SS-TOA/S-20/80: $f_{SS-TOA,0} = 0.23$; (b) SS-TOA/S-40/60: $f_{SS-TOA,0} = 0.43$; (C) SS-TOA/S-50/50: $f_{SS-TOA,0} = 0.50$; (d) SS-TOA/S-60/20: $f_{SS-TOA,0} = 0.63$. Refer to Table 5 for complete information. All GPC samples were prepared by dissolving in solvent system of 2wt% TOA in THF.

2.3.3 Determination of Copolymerization Reactivity Ratios

Table 5 summarizes the compositions for the copolymers synthesized from various initial feed compositions. To predict the copolymer composition in terms of the initial monomer concentrations, a terminal copolymerization model as proposed by Mayo^[84] was used.^[40,74] This model assumes the active site reactivity depends on the nature of the reactive terminus. It is characterized by reactivity ratios^[85-88] r_{SS-TOA} and $r_{Styrene}$, where r_{SS-TOA} is the relative preference for the SS-TOA monomer to add to a propagating chain with a terminal SS-TOA group, while ris the relative preference of the styrene monomer to add to a propagating chain with a terminal styrene group. Monomer reactivity ratios for SS-TOA and styrene were determined from NMR data via the Fineman-Ross^[85] and Kelen-Tüdös^[87,89] methods and by a nonlinear least-squares minimization fit (using MatLab with 95% confidence bound) to the Mayo-Lewis equation. The reactivity ratios are displayed in Table 6. The Mayo-Lewis plot is shown in Figure 10, using the reactivity ratios obtained from all three methods with our experimental data. Each provides a good fit to the experimental data and the slight variance between models is barely noticeable.

The larger reactivity ratio of SS-TOA compared to that of styrene reveals that the propagating SS-TOA radicals preferentially add to SS-TOA monomer rather than to styrene monomer. $r_{Styrene}$ is less than unity with the Fineman-Ross and the Kelen-Tüdös methods and is 1.19 by regression, but in all cases $r_{Styrene}$ is significantly lower than r_{SS-TOA} . The product of the reactivity ratios is also often used to suggest microstructure of the copolymer. As the product is larger than unity, the microstructure is likely to be "blocky".^[90] This has important implications, particularly in the development of gradient copolymers that can approximate the microstructure of block copolymers. For this particular system, with $r_{SS-TOA} >> r_{Styrene}$, the transition will be sharper as the polymerization proceeds, from a SS-TOA-rich part of the chain and once the SS-TOA is depleted, the copolymer will become predominantly richer in styrene segment.

Various styrene/neopentyl p-styrenesulfonate (SSPen) copolymers in organic solution were prepared by Okamura et al.^[62]. They report random copolymerizations for poly(S-ran-SSPen) using NMP at 120°C, but with azobis(isobutyronitrile)/2,2,5,5-tetramethyl-1-4-diethylphosphono-3-azahexane-3 nitroxide (AIBN/DEPN) initiators for SSPen molar feed composition of 33, 50 and 67 mol%. From the specified polymerization conditions and polymer properties for poly(S-ran-SSPen) with SSPen molar feed composition ranging from 33-67 mol%, reactivity ratios were evaluated using the Fineman-Ross and Kelen-Tüdös methods. The reactivity ratios were estimated as $r_{Styrene} = 1.28$, r_{SSPen} = 4.49 by Fineman-Ross and $r_{Styrene}$ = 1.33, r_{SSPen} = 4.61 by Kelen-Tüdös. Although the values cannot be closely compared to our data due to the different experimental conditions, they can be used as a general reference for reactivity between the two monomers. The reactivity ratios of SSPen are significantly larger than for styrene indicating the distinct preference for SSPen to add to itself. For this particular system, the value of SSPen is roughly 3.5 times ($r_{SSPen}/r_{Stvrene}$) more reactive than styrene, while for our system using NMP, the protected sulfonate monomer is roughly 6 times (average of the three methods used) more reactive than styrene. In both systems, styrenesulfonated monomer reactivity ratios found by Fineman-Ross and Kelen-Tüdös are ≈ 4.5 , whereas those of styrene are closer to unity ($r_{Styrene} = 0.74-0.77$ with our data and $r_{Styrene} = 1.28-1.33$ with Okamura et al.'s data); therefore, a similar conclusion can be drawn regarding the reactivity between the protected styrenesulfonated monomer and styrene.



Figure 10: Mayo-Lewis plot of copolymer composition with respect to *SS-TOA*, F_{SS-TOA} , versus monomer feed composition, $f_{SS-TOA,0}$, using *SS-TOA* and styrene reactivity ratios determined from Fineman-Ross and Kelen-Tüdös methods and from nonlinear least-squares fitting of the Mayo-Lewis equation to the experimental data ($r_{SS-TOA} = 4.43$ to 6.49 and $r_{Styrene} = 0.74$ to 1.10). The fits are indicated by the dashed lines while the experimental data for copolymerizations done in toluene at 110 °C using BlocBuilder as the unimolecular initiator and 8.5 mol % free nitroxide SG1 relative to BlocBuilder is indicated by the solid circles. The straight line indicates the azeotropic composition ($f_{SS-TOA} = F_{SS-TOA}$).

2.3.4 Gradient Polymerization of SS-TOA with GMA

A gradient polymerization of SS-TOA with GMA was performed to ensure a high concentration of sulfonate groups on one end of the chain. Based on its similar reactivity compared to styrene, SS-TOA was envisioned to be an effective controller for BlocBuilder mediated NMP of methacrylates using the co-monomer approach. ^[23,49] The GMA would then be added after a relatively low SS-TOA conversion was attained to gradually incorporate GMA into the polymer chain. Later processing, such as acid treatment, would remove the protecting group from the SS-TOA and aid in cross-linking the epoxy group inherent in GMA. From Figure 5, at a reaction temperature of 90 °C, SS-TOA conversion reached 25% after 220 min. Monomer conversion was determined using NMR from samples immediately before adding GMA and after 400 min, just before the polymerization was stopped. The results are summarized in Table 7. The molar ratio between unreacted SS-TOA and GMA at the injection time was reported as 0.01 (0.36 mmol SS-TOA/35 mmol GMA). Similarly, the samples were run in the GPC to characterize the molecular weight distribution just before and after GMA injection. The $M_{\rm p}$ increased from 2.1 kg·mol⁻¹ to 15.7 kg·mol⁻¹ while remaining monomodal and M_w/M_n increased from 1.28 to 1.43. From Figure 11, a clear shift was observed from the poly(SS-TOA) macroinitiator to the poly(SS-TOA-grad-GMA) copolymer after 400 min. These observations suggest that growth was occurring relatively steadily.



Figure 11: Gel permeation chromatogram of samples taken just before addition of glycidyl methacrylate (GMA) to SS-TOA (at 220 min) denoted by (-----) and at a later time (at 400 min) denoted by (----) for gradient polymerization at 90°C using poly(SS-TOA) as macroinitiator ($X_{SS-TOA} = 25\%$) to polymerize with GMA.

2.4 Conclusion

SS-TOA homopolymers and SS-TOA-*ran*-S copolymers of various SS-TOA/styrene mixtures were successfully synthesized by NMP. These materials were fully characterized with respect to kinetics, final polymer composition and molecular weight properties. Difficulties prevailed with the molecular weight characterization using GPC due to interactions of the sulfonate groups with the columns; although, the issue was reduced using a two-component solvent system of 2 wt% TOA in THF to completely dissolve the polymer samples. SS-TOA was polymerized in toluene at 90°C, 95°C, 100°C and 105°C by NMP using 8.5 mol% SG1 relative to BlocBuilder with target molecular weights of 20 kg·mol⁻¹ and 45 kg·mol⁻¹. Polymerizations were more controlled for theoretical molecular weight

experiments of 20 kg·mol⁻¹, giving polymers with M_w/M_n as low as 1.02 and a linear increase in M_n with conversion up to about 35%. This behaviour was not observed for higher theoretical molecular weights that could be indicative of chain transfer and other side reactions since more monomer is present relative to initiator and polymer. ^[80-82] The $\langle k_p \rangle \langle K \rangle$ values of SS-TOA were ~1.5-2 times greater compared to styrene homopolymerizations at the same temperature.

SS-TOA/styrene mixtures with SS-TOA molar feed composition, $f_{SS-TOA,0}$, ranging from 0.10-0.80 were copolymerized in toluene at 110°C with theoretical molecular weights at complete conversion near 30 kg·mol⁻¹, which resulted in monomodal molecular weight distributions ($M_n = 3.7-15.9 \text{ kg} \cdot \text{mol}^{-1}$) and low polydispersities ($M_w/M_n = 1.21-1.26$). Reactivity ratios for poly(SS-TOA-*ran*-S) were evaluated using Fineman-Ross, Kelen-Tüdös and nonlinear least-squares minimization methods. The copolymers were comparatively richer in SS-TOA for a given feed with reactivity ratios ranging from $r_{SS-TOA} = 4.43 \pm 0.16$ to $6.49 \pm$ 0.06 and $r_{Styrene} = 0.74 \pm 0.03$ to 1.10 ± 0.10 .

The effectiveness of SS-TOA as a controlling co-monomer for NMP was tested using a gradient polymerization of SS-TOA with GMA with NHS-BlocBuilder initiator at 90°C in toluene. Synthesis of poly(SS-TOA-*grad*-GMA) resulted in a monomodal molecular weight distribution with $M_w/M_n = 1.43$, suggesting SS-TOA behaves similarly to styrene as a controlling co-monomer for BlocBuilder-mediated NMP. The prepared sulfonated polymers and copolymers as amphiphilic precursors indicate NMP is a possible synthetic route towards achieving such materials for a number of applications such as templates for membranes.

2.5 Connection between manuscripts

The kinetic study of the SS-TOA homopolymers and SS-TOA/styrene copolymers, ($f_{SS-TOA,0} = 0.10-0.80$) led to the conclusion that it was possible with the help of the unimolecular initiator, BlocBuilder/SG1, to synthesize the sulfonate functional polymers with monomodal molecular weight distributions and low polydispersities ($M_w/M_n < 1.26$). The effectiveness of SS-TOA as a controlling co-monomer for NMP was successfully tested using an SS-TOA/GMA gradient polymerization with NHS-BlocBuilder initiator at 90°C, suggesting SS-TOA acts like styrene as a controlling co-monomer for BlocBuilder-mediated NMP. The analysis reveals that NMP is a possible synthetic route to produce these amphiphilic sulfonated polymeric materials for various applications, such as templates for membranes.

Acrylonitrile (AN) has also been shown to be an effective co-monomer for methacrylate polymerizations using BlocBuilder.^[91] Inclusion of AN in a styrenic resin provides good barrier properties while styrene (S) enhances processing behaviour.^[2] Poly(styrene-*ran*-acrylonitrile) (poly(S/AN)) resins possess outstanding mechanical properties, high heat distortion temperatures and excellent chemical resistance; properties all desirable for thermoplastic applications.^[92] In Section 3.0 of this thesis, S/AN copolymers with functional groups either on the

chain end or along the chain were examined using NMP as the synthetic route. These functional S/AN resins would be suitable candidates for blending into functional polyolefins for barrier applications.

3.0 Routes to Carboxylic Acid Functional Acrylonitrile Copolymers via Nitroxide Mediated Polymerization

Manuscript Abstract

Styrene/acrylonitrile (S/AN) copolymers were synthesized in 50 wt% 1,4-dioxane solutions at AN feed compositions, $f_{AN} = 0.10-0.86$, using two different unimolecular initiators, *N*-(2-methylpropyl)-*N*-(1-diethylphosphono-2,2dimethylpropyl)-O-(2-carboxylprop-2-yl) hydroxylamine (BlocBuilder) and a Nsuccinimidyl ester terminated BlocBuilder (NHS-BlocBuilder). In both systems, the polymers exhibited narrow molecular weight distributions and appeared monomodal in nature with low polydispersities $(M_w/M_n = 1.14-1.26)$, characteristic of a controlled polymerization. M_n versus conversion (X) plots were relatively linear ($M_n = 18.1 \text{ kg mol}^{-1}$, $X \approx 70\%$) suggesting that "pseudo-living" behaviour was approached. Tert-butyl methacrylate/acrylonitrile (t-BMA/AN) copolymers were synthesized at the same conditions as S/AN at AN feed compositions, $f_{AN} = 0.10-0.80$, using both BlocBuilder (with 8.0-8.5 mol% Ntert-butyl-N-(1-diethyphosphono-2,2-dimethylpropyl) nitroxide (SG1) relative to BlocBuilder) and NHS-BlocBuilder as unimolecular initiators. In both systems, the polymers usually exhibited narrow molecular weight distributions and appeared monomodal in nature with $M_w/M_n = 1.17$ -1.50. M_n versus conversion (X) plots were relatively linear up to reasonably high conversion ($M_n = 15.6 \text{ kg} \text{ mol}^{-1}$, $X \approx 60\%$,) for both BlocBuilder and NHS-BlocBuilder initiated systems. The reactivity ratios for S/AN copolymerizations were $r_{AN} = 0.07 \pm 0.01$ to 0.11 ± 0.01 and $r_S = 0.27 \pm 0.02$ to 0.42 ± 0.03 ; for *t*-BMA/AN copolymerizations they were $r_{AN} = 0.07 \pm 0.01$ to 0.14 ± 0.03 and $r_{t-BMA} = 0.89 \pm 0.19$ to 1.28 ± 0.15 . The reactivity ratios were similar using either BlocBuilder or NHS-BlocBuilder initiator, and were in agreement with previous literature.

3.1 Manuscript Introduction

Products such as gasoline and other pure or mixed hydrocarbon solvents, as well as gas molecules, can easily permeate polyethylene (PE) containers resulting in pollution, safety and health problems.^[93] To overcome these permeability problems, appropriate polymer blending into PE is done to develop barrier morphologies that act as barriers.^[44,93,94] Multiphase polymer blends are of high commercial interest due to the possibility of combining features and improving material properties; however, most polymer blends are immiscible and tend to phase-separate when combined.^[5,7] The poor miscibility of the two components leads to inferior mechanical properties. To overcome these limitations, a compatibilizer is added to stabilize one polymer with another.^[95,96] The most common way to compatibilize multiphase blends is through reactive polymer blending, where the individual homopolymers are functionalized prior to melt-

blending which then form a copolymer at the interface during melt-blending.^[97-99] The interfacial compatibilization leads to greater interfacial adhesion, with smaller dispersed phase domains. The compatibilizing agent also prevents the recombination of the minor-phase droplets by coalescence and thus the morphology can be stabilized.^[100] This cost-effective technique is widely employed, as polymer components can be blended more effectively due to homogeneous particle dispersion which also often leads to desired material properties.^[99]

Reactive polymer blending has been used to produce morphologies needed for barrier applications.^[43] For example, nylon is compounded into PE for gas tanks where the nylon is dispersed as laminar structures in the matrix to serve as a barrier to prevent swelling of the polyolefin.^[44] Such morphologies of nylon within the polyolefin matrix are stabilized by reactive blending between the amino groups in the nylon and complementary functional groups like maleic anhydride that are grafted onto the polyolefin.^[45] The resulting copolymer formed reactively at the interface during melt-blending prevents the coalescence of the dispersed nylon phase during processing, such as rotational or injection molding (see Figure 12). This approach is limited to commercially available polymers with the inherent functionality (nylon has terminal primary amine groups). To produce a wider range of barrier materials to be applied in several applications, it is desirable to include polymers where the functional group is not a direct residue of the original polymerization process. It may also be beneficial to place a single functional group at the chain end or to restrict the functional groups to one part of the chain, as the placement of functional groups has a dramatic effect on the reactivity and thus on the blend morphology.^[101]



Figure 12: Reactive polymer blending for compatibilizing polymer blends

This study examines a unique approach to widen the applicable polymers for barrier materials while using desirable polymerization processes currently in common industrial practice: free radical polymerization technology. The aim is to investigate the development of new barrier polymers based on poly(styrene-*ran*acrylonitrile) copolymers (poly(S/AN)) that have functional groups either on the chain end or along the chain. S/AN-type copolymers have long been used due to excellent grease resistance, and oxygen and carbon dioxide barrier properties at higher acrylonitrile loadings.^[79] Controlled radical polymerization (CRP) can be used to achieve the desirable placement of functional groups. CRP is an attractive polymerization method, since it approaches the narrow molecular weight distribution and the ability to control microstructure attained using "living" or ionic polymerizations, without the need of air-free transfers, careful purification of reagents and functional group protection typically required of the latter.^[12]

The immiscible polymers (S/AN and PE) can be coupled using the amine/anhydride^[43,98] reaction or by the carboxylic acid/epoxy reaction^[97] (Figure 13), since those groups can be easily introduced into the polymers and have been used in commercial blend systems.^[102] The amine/anhydride coupling reaction has been characterized as the most effective in reactive blending; although, in previous literature, carboxylic acids have shown to be readily introduced into resins using CRP.^[19] Commercially available PE grafted with anhydride or epoxy groups are logical choices for the initial matrix materials. In this way, the resulting amino functional or carboxylic acid functional S/AN copolymers can later be melt-blended with the anhydride or epoxy grafted PE in a twin-screw extruder to study the morphology as a function of composition, rheology and processing conditions of the dispersed domains. After more extensive permeability testing, processing and mechanical testing, such materials can possibly be developed for future PE-based barrier materials. These initial designs can be later used as starting points for future designs to impart more sophisticated microstructures due to the control attainable by NMP.

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Figure 13: Reactions between (top) a cyclic anhydride and a 1° amine to first yield amic acid, and after condensation, an imide and between (bottom) carboxylic acid and epoxy groups to yield an ester.

3.1.1 Preparation of Carboxylic Acid Functional and Amino Functional Poly(styrene-ran-acrylonitrile) (S/AN) via NMP

S/AN resins possess many physical properties desired for thermoplastic applications. They are hard, rigid and stable with good load-bearing capabilities, have high heat distortion temperatures and excellent chemical resistance. Inclusion of acrylonitrile (AN) in the resin is important as it provides the barrier properties while styrene (S) provides better processing behaviour.^[2] The S/AN materials chosen will be amino functional or carboxylic acid functional by suitable nitroxide mediated copolymerization (NMP). NMP is desirable due to its simplicity, particularly when using unimolecular initiators such as *N*-(2-methylpropyl)-*N*-(1-diethylphosphono-2,2-dimethylpropyl)-*O*-(2-carboxylprop-2-yl) hydroxylamine (BlocBuilder, commercially available from Arkema, Inc.)^[34].

Thus, the following study focused on testing the amenability of NMP to polymerize S/AN with the functional groups located on the chain end or pendant along the backbone, allowing for a better control of morphology and physical properties.

There is significant literature on S/AN copolymerizations by $CRP^{[29,37]}$ ^{103,104,105,106,]} but limited ranges of S/AN feed compositions have been studied by NMP and none have been specifically copolymerized using BlocBuilder (Figure 14). Thus, S/AN copolymerization using BlocBuilder must be explored to determine how much AN can be incorporated into the copolymer for a given feed composition. Figure 15 shows that a moderate increase in AN incorporation can significantly reduce O₂ and CO₂ permeability in the S/AN copolymer, thereby improving barrier properties.^[79]



Figure 14: Structure of a) BlocBuilder and b) SG1



Figure 15: O₂ and CO₂ permeability in the S/AN copolymer as a function of acrylonitrile (AN) content.^[79]

Carboxylic Acid and Amino Functional S/AN

Both S and AN have been polymerized by NMP independently^[91]. Here, S, AN and *tert*-butyl methacrylate (*t*-BMA) were polymerized using BlocBuilder, as either binary or ternary copolymerizations with the functional protected acid units from *t*-BMA incorporated at different locations on the chain as shown in Figure 16. S/AN terminated with a single carboxylic acid group (S/AN-COOH) can be accessed from the initiator residue of the BlocBuilder mediator (Route *A* in Figure 16). Route *B* involves the terpolymerization of S, AN and *t*-BMA to produce S/AN with random carboxylic acid functionality (after deprotection of the *tert*-butyl group) (S*-ran*-AN-*ran*-COOH). Acrylic acid is known to degrade the alkoxyamine group (SG1) during the polymerization and make the chain end inactive and unable to initiate a second block. Significantly lower probabilities of intramolecular reactions (backbiting) or chain transfer reactions during polymerization are present with methacrylates compared to acrylates, thus the use

of the protected organo-soluble methacrylic acid, *tert*-butyl methacrylate, was preferred to avoid side reactions that could possibly alter the desired microstructure.^[49,107] Additionally, the use of *tert*-butyl methacrylate was desirable to minimize the degradation of the methacrylic acid with the alkoxyamine (SG1).^[49,107] The *tert*-butyl methacrylate can be cleaved postpolymerization to yield the acid-containing copolymer.



Figure 16: Routes for carboxylic acid functional styrene-*ran*-acrylonitrile (S/AN) copolymers using nitroxide-mediated polymerization (NMP) with BlocBuilder.

Incorporating monomers with primary amine functionality is potentially challenging using BlocBuilder. Having the carboxylic acid group in the BlocBuilder structure was initially thought to be problematic for amino group incorporation as it can interfere and perhaps react with the carboxylic acid at the relatively high temperatures used for polymerization. Thus, we attempted a protection scheme that has been developed based on recent literature to render BlocBuilder incapable of interacting with the functional monomer. The BlocBuilder initiator was reacted with *N*-hydroxysuccinimide (NHS) to yield the inimidyl ester terminated BlocBuilder shown in Figure 17a. NHS-BlocBuilder is an attractive molecule as it can be convenient for the functionalization of polymer chain ends post-polymerization. Figure 17b shows the S/AN copolymerization (similar to Route *A* in Figure 16) using NHS-BlocBuilder, which can be converted to a single amine terminated S/AN by reaction with excess diamine.

It has also shown to be an efficient initiator for styrene and *n*-butyl acrylate polymerizations without the need of additional SG1.^[68] Since the dissociation constant is roughly 15 times higher than that of BlocBuilder, sufficient free SG1 is released by the NHS-BlocBuilder to effectively control the polymerizations.^[68] This feature has recently been reported for methacrylate polymerizations (glycidyl methacrylate/styrene copolymerizations in particular) with NHS-BlocBuilder,^[108] which typically require ~ 10 mol% excess SG1 relative to BlocBuilder initially for a controlled polymerization.^[109] We thus expect that the NHS can serve as a protecting group that can later be transformed

to produce amine-functional S/AN copolymers (Figure 17), as well as to sufficiently release enough SG1 from the start of the reaction to control *t*-BMA-richh polymerizations (*t*-BMA/AN copolymers and S/AN/*t*-BMA terpolymers).



Figure 17: a) Synthetic scheme to convert the carboxylic acid functional BlocBuilder initiator into the protected *N*-succinimidyl ester form. b) styrene-*ran*-acrylonitrile (S/AN) copolymers using nitroxide-mediated polymerization (NMP) with NHS-BlocBuilder; the route towards producing single amine terminated S/AN upon reaction with excess diamine.

3.2 Experimental

3.2.1 Materials

Acrylonitrile (99%), styrene (99%) and *tert*-butyl methacrylate (98%) were purchased from Sigma-Aldrich and purified by passing through a column of basic

alumina (Brockmann, Type 1, 150 mesh) mixed with 5% calcium hydride (90-95%, reagent grade), then sealed with a head of nitrogen and stored in a refrigerator until needed. Hexane (98.5%), methanol (99.8%) tetrahydrofuran (99.9%) and 1,4-dioxane (99.8%) were obtained from Fisher and used as received. N-(2-methylpropyl)-N-(1-diethylphosphono-2,2-dimethylpropyl)-O-(2-

carboxylprop-2-yl) hydroxylamine (BlocBuilder[®], 99%) was obtained from Arkema and N-*tert*-butyl-N-[1-diethyl phosphono-(2,2-dimethylpropyl)] nitroxide (SG1, 85%) was kindly donated by Noah Macy of Arkema and used as received. *N*-hydroxysuccinimide (98%) and *N*,*N*'-dicyclohexylcarbodimide (DCC, 99%) were received from Sigma-Aldrich and used in conjunction with BlocBuilder to synthesize the *N*-succinimidyl ester terminated alkoxyamine BlocBuilder (NHS-BlocBuilder) using the same procedure as Vinas et al.^[68] Poly(styrene) (PS, M_n = 13.0 kg^{-mol⁻¹}, M_w/M_n = 1.10), poly(AN) (M_n = 60.6 kg^{-mol⁻¹}, M_w/M_n = 1.70), and poly(*t*-BMA) (M_n = 38.5 kg^{-mol⁻¹}, M_w/M_n = 1.01) were used as standards for Fourier transform infrared spectroscopy (FTIR) and were obtained from Scientific Polymer Products Inc.

3.2.2 Synthesis of Styrene/Acrylonitrile Random Copolymers (poly(S/AN))

Several nitroxide mediated copolymerization experiments of styrene (S) and acrylonitrile (AN) in 1,4-dioxane were conducted at 90°C using both BlocBuilder and NHS-BlocBuilder. All copolymerizations were performed in a 50 mL three-neck round bottom glass flask equipped with a magnetic stir bar, condenser and

thermal well. The flask was set inside a heating mantle and placed on a magnetic stirrer. Formulations for initial molar feed compositions, $f_{AN,0}$, from 0.10-0.70 were followed and are found in Table 8 and Table 9. All polymerizations were conducted in 50 wt% 1,4-dioxane solutions (50 wt% of monomer in solvent). The target molecular weight $(M_{n,target})$ at complete conversion, calculated by the mass of monomer relative to the moles of BlocBuilder or NHS-BlocBuilder initiator, was set to approximately 25 kg·mol⁻¹ in all cases. Initiator, solvent and monomer were added to the flask with the stirrer. As an example, for the synthesis of S/AN-BB-30, BlocBuilder (0.102 g, 0.267 mmol) and the stirrer were added to the flask, which was then sealed with a rubber septum. Styrene (5.6 g, 0.0538 mol), acrylonitrile (1.22 g, 0.0230 mol) and 1,4-dioxane (6.8 g, 0.0772 mol) were each injected into the flask. The central neck was connected to a condenser and capped with a rubber septum with a needle to relieve pressure applied by the nitrogen purge throughout the reaction. A thermocouple was connected to a controller and inserted into the third neck of the flask. As stirring began and the monomers were well mixed, the chilling unit (Neslab 740) using a glycol/water mixture that is connected to the condenser was set to 5°C. A nitrogen flow was introduced to purge the solution for 30 minutes. The reactor was heated to 90°C at a rate of about 5°C·min⁻¹ while maintaining the purge. Once the reaction reached the setpoint temperature, the first sample was taken (t = 0, start of the reaction) with a 1 mL syringe followed by periodic sampling until the solution became too viscous to withdraw from. The samples were precipitated in hexane, left to settle for

several hours, then decanted and dried overnight in a vacuum oven at 60°C. In particular, for the synthesis of S/AN-BB-30, the final yield after 240 minutes was 3.41 g (50% conversion based on gravimetry) with number-average molecular weight $M_n = 16.6 \text{ kg} \cdot \text{mol}^{-1}$, weight average molecular weight $M_w = 19.4 \text{ kg} \cdot \text{mol}^{-1}$ and polydispersity index of $M_w/M_n = 1.17$ determined by gel permeation chromatography calibrated relative to linear PMMA standards in DMF at 50°C and corrected with composition averaged Mark-Houwink parameters.

3.2.3 Synthesis of tert-Butyl Methacrylate/Acrylonitrile Random Copolymers (poly(t-BMA-ran-AN))

Nitroxide mediated copolymerizations of *tert*-butyl methacrylate (*t*-BMA) and (AN) in 1,4-dioxane were conducted at 115°C using both BlocBuilder and NHS-BlocBuilder. All copolymerizations were performed in a 50 mL three-neck round bottom glass flask equipped with a magnetic stir bar, condenser and thermal well. The flask was set inside a heating mantle and placed on a magnetic stirrer. Formulations for initial molar feed compositions, $f_{AN,0}$, from 0.10-0.80 were followed and are found in Table 10 and Table 11. All polymerizations were conducted in 50 wt% 1,4-dioxane solutions (50 wt% of monomer in solvent). Target molecular weights at complete conversion ($M_{n,target}$), calculated based on the mass of *t*-BMA and AN monomers relative to BlocBuilder or NHS-BlocBuilder initiator, were nearly 25 kg·mol⁻¹ for all experiments. In this case, for experiments conducted using BlocBuilder initiator, 8.1-8.5 mol% SG1 free nitroxide relative to BlocBuilder was used to help control the polymerization with

the methacrylic monomer (no additional SG1 was used with NHS-BlocBuilder as the initiator). Initiator, solvent and monomer were added to the flask with the stirrer. As an example, for experiment ID t-BMA/AN-BB-30, BlocBuilder (0.0975 g, 0.256 mmol) was added to the flask, which was then sealed with a rubber septum. *t*-BMA (5.58 g, 0.0392 mol), acrylonitrile (0.908 g, 0.0171 mol) and 1,4-dioxane (6.40 g, 0.0726 mol) were each injected into the flask using disposable 5 mL syringes to accurately obtain the required feed compositions. The central neck was connected to a condenser and capped with a rubber septum with a needle to relieve pressure applied by the nitrogen purge throughout the reaction. A thermocouple was connected to a controller and inserted into the third neck of the flask. As stirring began and the monomers were mixed, the chilling unit (Neslab 740) using a glycol/water mixture that is connected to the condenser was set to 5°C. A nitrogen flow was introduced to purge the solution for 30 minutes. The reactor was heated to115°C at a rate of about 5°C·min⁻¹ while maintaining the purge. Once the reaction reached the set-point temperature, the first sample was taken (t = 0, start of the reaction) with a 1 mL syringe followed by periodic sampling until the solution became too viscous to withdraw from. The samples were precipitated in a 70% w/w methanol/distilled water mixture, left to settle for several hours, then decanted and dried overnight in a vacuum oven at 60°C. In particular, for the synthesis of t-BMA/AN-BB-30 the final yield after 350 minutes was 3.61 g (55% conversion based on gravimetry) with number-average molecular weight $M_n = 10.4 \text{ kg} \cdot \text{mol}^{-1}$, weight average molecular weight $M_w =$

14.1 kg·mol⁻¹ and polydispersity index of $M_w/M_n = 1.35$ determined by gel permeation chromatography calibrated with linear poly(styrene) standards in THF at 40°C and corrected with composition averaged Mark-Houwink parameters.

3.2.4 Synthesis of tert-Butyl Methacrylate/Styrene/Acrylonitrile Random Terpolymers (poly(t-BMA-S-AN))

A nitroxide mediated terpolymerization experiment of *tert*-butyl methacrylate, styrene and acrylonitrtile in 1,4-dioxane was conducted at 90°C. A similar procedure used for the S/AN and t-BMA/AN copolymerizations described in detail above was followed. t-BMA (1.83 g, 0.0183 mol), styrene (5.20 g, 0.0499 mol) and AN (3.40 g, 0.0641 mol) were each injected in the flask with a Nhydroxysuccinimide terminated BlocBuilder (NHS-BlocBuilder) in a 50 wt% solution of 1,4-dioxane (Table 12). We seek to determine whether NHS-BlocBuilder would be an effective controller for *t*-BMA/S/AN terpolymerization without any added free nitroxide. Over the course of the reaction, samples were taken periodically with a 1 mL syringe and precipitated in hexane. The samples were left to settle for several hours, decanted and then dried overnight in a vacuum oven at 60°C. The final yield after 450 minutes was 5.59 g (54% conversion based on gravimetry) with number-average molecular weight M_n = 13.5 kg·mol⁻¹, weight average molecular weight $M_{\rm w} = 16.1$ kg·mol⁻¹ and polydispersity index of $M_w/M_n = 1.19$ determined by gel permeation chromatography calibrated with linear poly(styrene) standards in THF at 40°C and corrected with composition averaged Mark-Houwink parameters.

3.2.5 Characterization

The molecular weight and molecular weight distribution of the copolymers were characterized by gel permeation chromatography (GPC) using a Waters Breeze system equipped with three Styragel columns (molecular weight ranges: HR1: 10^2 - 5×10^3 g·mol⁻¹, HR2: 5×10^2 - 2×10^4 g·mol⁻¹, HR3: 5×10^3 - 6×10^5 g·mol⁻¹) and a guard column heated to 50°C during analysis. Dimethylformamide (DMF) was used as the mobile phase for S/AN copolymers as the polymers were not fully soluble in THF with relatively high AN loadings (\approx 52 mol% AN) and tetrahydrofuran (THF) was used as the mobile phase for *t*-BMA/AN copolymers (the copolymers were soluble as AN loadings were below $\approx 35 \text{ mol}\%$) each with an applied flow rate of 0.3 mL·min⁻¹ during analysis. The GPC was also equipped with ultraviolet (UV 2487) and differential refractive index (RI 2410) detectors. The molecular weights were reported relative to calibration with linear, narrow molecular weight distribution poly(styrene) standards (when using THF) and poly(methyl methacrylate) standards (when using DMF). The copolymer molecular weights were corrected using the Mark-Houwink relationship $[\eta] =$ KM^{α}, based on the following coefficients: $K_{PS} = 11.4 \times 10^{-5} \text{ dLg}^{-1}$ and $\alpha_{PS} = 0.716$ in THF at 40°C; $^{[110]}$ $K_{Pt-BMA} = 11.2 \times 10^{-5} \text{ dLg}^{-1}$ and $\alpha_{Pt-BMA} = 0.692$ in THF at 30° C;^[111] $K_{PAN} = 21.2 \times 10^{-5} \text{ dL} \text{g}^{-1}$ and $\alpha_{PAN} = 0.75$ in DMF at 60°C (data at 50°C)

was not available).^[112] For the PMMA standards used in DMF, $K_{PMMA} = 2.07 \times 10^{-5} dL'g^{-1}$ and $\alpha_{PMMA} = 0.632$ in DMF at 50°C.^[75] The molecular weights were corrected by compositionally averaging the Mark-Houwink coefficients for the copolymers and then correcting appropriately against the pure poly(methyl methacrylate) (PMMA) standards for the S/AN copolymers and against the pure poly(styrene) standards for the *t*-BMA/AN copolymers. Fourier transform infrared spectroscopy (FTIR) (Spectrum BX, Perkin-Elmer) was used to determine the molar composition of the copolymers and the terpolymer. The peak absorbances at 1460 cm⁻¹, 2200 cm⁻¹, 1200 cm⁻¹ were used as markers for S, AN and *t*-BMA, respectively. To precisely identify the copolymer compositions 6-point calibration curves were constructed with mixtures of poly(S), poly(AN) and poly(*t*-BMA) standards. All reactivity ratio determinations were done using samples that were polymerized to low conversion (<10%) to avoid compositional drift corrections.

3.3 Results

3.3.1 Styrene/Acrylonitrile Random Copolymers (poly(S/AN)) using BlocBuilder Initiator

The unimolecular initiator, BlocBuilder (structure shown in Figure 14) has inherent carboxylic acid (COOH) group functionality, and thus it can impart a single COOH group at the chain end to be used in reaction with epoxy groups. The first challenge was to understand how AN polymerizations could be controlled via BlocBuilder. It is important to note that in contrast to TEMPO-

mediated systems, unimolecular initiators like BlocBuilder can easily control styrenic polymerizations without any additional free radical initiator. Literature suggested AN can be incorporated into resins via NMP, although in relatively low concentrations and without reporting much detail.^[37] The amount of AN that can be incorporated into S/AN resins was studied to establish whether the resin would be useful for barrier applications as higher AN molar composition in copolymer, $F_{AN} > 0.40-0.50$ provides better barrier properties.^[79] Various S/AN mixtures were synthesized by examining NMP with BlocBuilder, using our previous experience with S polymerizations by NMP as a guide.^[75,113] At 90 °C in 50 wt% 1.4-dioxane solution, S/AN mixtures up to an AN molar feed concentration, $f_{AN,0}$ = 0.70 were polymerized with BlocBuilder, without using any additional SG1 free nitroxide as a mediator. The polymerization rates did not vary significantly as AN feed content increased, as shown in Figure 18 by the semi-logarithmic plot of scaled conversion $(ln(1-X)^{-1})$ where X = monomer conversion) versus time. Note that the apparent rate constant, obtained from the slope in the linear range of Figure 18, $\langle k_p \rangle [P \cdot]$ (where $\langle k_p \rangle$ is the average propagation rate constant and [P·] is the concentration of propagating radicals) decreased slightly from $(5.2 \pm 0.8) \times$ 10^{-5} to $(3.0 \pm 0.2) \times 10^{-5}$ s⁻¹ with increasing feed composition ($f_{AN,0} = 0.10-0.70$). This is reasonable as recently published data for the propagation rate constant, k_p , of AN $(k_{p,AN} = 1.1 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1})^{[114]}$ suggests it is nearly an order of magnitude higher compared to the homopropagation rate constant for styrene ($k_{p,S} = 1.8 \times 10^3$ L mol⁻¹ s⁻¹) at 90°C.^[115] The literature estimates for the equilibrium constant K

between the dormant and active SG1-capped chains are however comparable. For styrene homopolymerizations, $K_s = 4 \times 10^{-10}$ mol L⁻¹ at 90°C^[31] and for acrylonitrile homopolymerizations, $K_{AN} = 1 \times 10^{-11}$ mol L⁻¹ ^[116] which was estimated from K for n-butyl acrylate^[31]. The counterbalance effect found from combining $\langle k_p \rangle$ and $\langle K \rangle$ can be summarized using the penultimate model to reasonably predict $\langle k_p \rangle [P \cdot]$ with literature data available for S/AN conventional radical copolymerizations. The $\langle k_p \rangle$ based on the penultimate model is given by the following expression^[117]:

$$\left\langle k_{p} \right\rangle = \frac{r_{AN} f_{AN}^{2} + 2f_{AN} f_{S} + r_{s} f_{S}^{2}}{r_{AN} \frac{f_{AN}}{k_{p,AN}} + r_{S} \frac{f_{S}}{k_{p,S}}}$$
(7)

where:

$$\overline{k_{p,AN}} = k_{p,AN} \frac{r_{AN} f_{AN} + f_S}{r_{AN} f_{AN} + \frac{f_S}{s_{AN}}}; \quad \overline{k_{p,S}} = k_{p,S} \frac{r_S f_S + f_{AN}}{r_S f_S + \frac{f_{AN}}{s_S}}$$
(8)

Note that the molar feed fractions for AN and S are given by f_{AN} and $f_S = 1 - f_{AN}$, respectively. The monomer reactivity ratios are given by r_{AN} and r_S , and the radical reactivity ratios are given by s_{AN} and s_S , for AN and S respectively. The concentration of propagating macroradicals for a system controlled by a free radical like SG1 is given by^[17]:

$$[P \cdot] = \left(\frac{K[I]_0}{3k_t}\right)^{1/3} t^{-1/3}$$
(9)

where $[I]_0$ is the initial concentration of BlocBuilder nitroxide initiator, t is the time, $\langle k_t \rangle$ is the average termination rate constant and $\langle K \rangle$ is the average equilibrium constant for the penultimate model^[23]:

$$\left\langle K \right\rangle = \frac{\frac{r_{AN}f_{AN}}{k_{p,AN}} + \frac{r_{S}f_{S}}{k_{p,S}}}{\frac{r_{AN}f_{AN}}{\overline{k}_{p,AN}K_{AN}} + \frac{r_{S}f_{S}}{\overline{k}_{p,S}K_{S}}}; \qquad \left\langle k_{t} \right\rangle = \left(p_{S}k_{t,S}^{1/2} + p_{AN}k_{t,AN}^{1/2}\right)^{2}$$
(10)

The parameters $p_{\rm S}$ and $p_{\rm AN}$ are given by:

$$p_{s} = \frac{\frac{r_{s}f_{s}}{k_{p,s}}}{\frac{r_{AN}f_{AN}}{k_{p,AN}} + \frac{r_{s}f_{s}}{k_{p,s}}} and p_{AN} = 1 - p_{s}$$

$$\tag{11}$$

The homo-termination rate constant for S is $k_{t,S} = 1.3 \times 10^8$ L mol⁻¹ s⁻¹ at 90°C^[118], while for AN it is $k_{t,AN} = 9.2 \times 10^9$ L mol⁻¹ s⁻¹ from the expression presented by Keramopoulos and Kiparissides^[119] with $k_{t,AN} = 1.98 \times 10^{-5400/RT}$ e¹⁴ (R = gas constant, T= temperature (K)). The monomer and radical reactivity ratios used for the penultimate model were taken from Hill et al from data at 60 °C, since data at 90°C was not available.^[120] The values are: $r_{AN} = 0.039$, $r_{S} = 0.22$, $s_{AN} = 0.229$ and $s_{S} = 0.634$. From *Equation 10* and *Equation 11*, the literature data can be used to predict a $\langle k_p \rangle [P \cdot]$ for S/AN copolymerization by NMP as a comparison to experimental data. As the [P[·]] term is time dependent, it was plotted for each composition as a function of time, which decreased and leveled at a relatively constant value (estimated as 2 x 10³ s⁻¹) taken as the steady state [P[·]]. It can be seen from Figure 19, that the plots of experimental results and predicted apparent rate constants as a function of $f_{AN,0}$ do not match very closely but the variation of $\langle k_p \rangle [P \cdot]$ with composition is not wide.



Figure 18: Kinetic plots of styrene/acrylonitrile (S/AN) copolymerizations with BlocBuilder at 90 °C in 50 wt% 1,4-dioxane as a function of molar feed composition of AN: $f_{AN,0} = 0.10$ (\Box), 0.30 (\triangle), 0.40 (\diamondsuit), 0.50 (\blacksquare) and 0.70 (\bullet). The slopes from the linear regions provide the apparent rate constants $k_p[P^{-}]$ which are plotted as a function of $f_{AN,0}$ in Figure 19



Figure 19: Apparent rate constants $\langle k_p \rangle [P \cdot]$ (where $\langle k_p \rangle$ is the average propagation rate constant and [P[·]] is the concentration of propagating macroradicals) for styrene/acrylonitrile (S/AN) copolymerizations versus initial AN feed composition, $f_{AN,0}$, using BlocBuilder (\bullet) at 90 °C in 50% 1,4-dioxane solution.

To determine the control of the copolymerization, the molecular weight distributions (MWD) were obtained via GPC and used with the kinetic data to obtain plots of number average molecular weight (M_n) versus conversion (X). The characteristics of the S/AN copolymers controlled with BlocBuilder are displayed in Table 13. The polymers exhibited a narrow molecular weight distribution and appear monomodal in nature (Figure 20) with low polydispersities ($M_w/M_n = 1.17$ -1.26), suggestive of a controlled polymerization. The MWD shifted to lower

elution times as the molecular weight of the polymers increased. An M_n versus X plot is useful to see how closely the CRP mimics truly "living" polymerizations, which theoretically have no termination reactions and would thus be linear. Figure 21 shows the plot of M_n versus X for BlocBuilder controlled S/AN copolymerizations at various initial AN molar feed compositions, $f_{AN,0}$. Note that the straight, solid line is the theoretically expected M_n versus X behaviour. It should be noted that the GPC was run using PMMA standards in DMF solvent and thus corrections were necessary using appropriate Mark-Houwink coefficients.^[110,112] For S/AN copolymers, compositionally averaged Mark-Houwink parameters were used to estimate the actual molecular weight of the copolymers. Mark-Houwink parameters for poly(styrene) were not available in DMF; thus the corrections may not necessarily be perfect. Still, the plots were relatively linear up to $\approx 40\%$ conversion ($M_n = 16.0 \text{ kg mol}^{-1}$) suggesting that a "pseudo-living" behaviour was approached up to that point.



Figure 20: Gel permeation chromatograms of samples taken at various times for S/AN copolymerizations (denoted by S-*ran*-AN) performed in 50 wt% 1,4dioxane solution at 90 °C with target molecular weights at complete conversion of 25 kg·mol⁻¹ and with different monomer feed concentrations using BlocBuilder initiator. The experiments are denoted as S/AN-BB-XX, where XX represents the initial molar feed concentration of AN given by f_{AN} : (a) S/AN-BB-10, $f_{AN,0} = 0.10$; (b) S/AN-BB-30, $f_{AN,0} = 0.30$; (C) S/AN-BB-50, $f_{AN,0} = 0.50$; (d) S/AN-BB-70, $f_{AN,0} = 0.70$. The GPC was performed in DMF at 50 °C using PMMA standards.


Figure 21: Number average molecular weight (M_n) versus conversion (X) for styrene/acrylonitrile (S/AN) copolymerizations performed in 50 wt% 1,4-dioxane solution at 90 °C with target molecular weights at complete conversion of 25 kg·mol⁻¹, using BlocBuilder with various AN molar feed compositions: $f_{AN,0} = 0.10 \ (\Box), 0.30 \ (\Delta), 0.40 \ (\diamondsuit), 0.50 \ (\blacksquare)$ and 0.70 (\bullet) .

The final molar composition of the various copolymers under study were determined using FTIR and are presented in Table 13. The final molar composition of AN, F_{AN} , shows that at low $f_{AN,0}$ the molar composition of AN was significantly richer than that of the feed while at high $f_{AN,0}$ ($f_{AN,0} > 0.50$), the copolymer composition became increasingly less rich in AN compared to the feed. For example, in experiment ID S/AN-BB-50 and S/AN-BB-70 with $f_{AN,0}$ of 0.50 and 0.70, respectively, the copolymer compositions, F_{AN} , were 0.46 and 0.52,

respectively. From Figure 15, it is suggested that F_{AN} between 0.40 to 0.66 (25-50 wt% AN) should be sufficient to reduce O_2 and CO_2 permeability in the S/AN copolymer for sufficiently effective barrier properties; thus this can be achieved at $f_{AN,0} > 0.30$.^[79]

3.3.2 Styrene/Acrylonitrile Random Copolymers (poly(S/AN)) using NHS-BlocBuilder Initiator

NHS-BlocBuilder has been an effective controller for styrene and *n*-butyl acrylate polymerizations without additional free nitroxide required.^[68] We started studying its suitability for S/AN copolymerizations, beginning with experiments at 115 °C in 50 wt% 1,4-dioxane solutions without any added free nitroxide. S/AN copolymerizations were sufficiently controlled by BlocBuilder alone (Section 3.3.1) and thus copolymerizations with NHS-BlocBuilder would serve as a good comparison to test its effectiveness. Figure 22 shows the semi-logarithmic plots of $ln(1-X)^{-1}$ versus time of S/AN copolymerizations with $f_{AN,0} = 0.13-0.86$. All plots are linear and extraction of the apparent rate constants, $\langle k_p \rangle [P \cdot]$, from such plots indicate that increasing AN feed content tended to slightly vary the $k_p[P] = (4.0 \pm$ 0.1 × 10⁻⁵ at $f_{AN,0} = 0.13$ to $k_p[P] = (6.8 \pm 0.5) \times 10^{-5} \text{ s}^{-1}$ at $f_{AN,0} = 0.86$, which is in the range with that reported for S/AN copolymerizations using BlocBuilder in Section 3.3.1 (except for that the temperature was higher). There was not expected to be a great variation of the kinetics with increasing AN feed content. The homopropagation rate constants at 115°C were estimated as $k_{p,AN} = 1.5 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$ ^[114] and $k_{p,s} = 1.8 \times 10^3 \text{ L mol}^{-1} \text{ s}^{-1[115]}$. As for the equilibrium constant K, for S by

NMP with SG1-type initiators, $K_S \approx 2.2 \times 10^{-9}$ mol L^{-1[31]}, while AN was approximated to be similar to n-butyl acrylate, $K_{AN} \approx 1 \times 10^{-10}$ mol L⁻¹ at 115°C^[116]. The $\langle k_p \rangle \langle K \rangle$ is related to $\langle k_p \rangle [P \cdot]$ given certain assumptions and is normally used to measure the control of NMP.^[116,47] The combined parameter $k_p K$ for S and AN available in the literature at 115°C: $(k_p K)_S \approx 4 \times 10^{-6} \text{ s}^{-1}$ and $(k_p K)_{AN}$ $\approx 2 \times 10^{-6} \text{ s}^{-1}$, can compared against the experimental data. The literature data mirrors the trend in $\langle k_p \rangle [P \cdot]$ observed for the S/AN copolymerizations using NHS-BlocBuilder with the change in feed composition $f_{AN,0}$ as shown in Figure 23.



Figure 22: Kinetic plots of styrene/acrylonitrile (S/AN) copolymerizations with NHS-BlocBuilder at 115 °C in 50 wt% 1,4-dioxane solution for AN molar feed compositions: $f_{AN,0} = 0.13$ (\Box), 0.20 (O), 0.30 (\triangle), 0.39 (\diamondsuit), 0.52 (\blacksquare), 0.70 (\bigcirc) and 0.86 (\blacklozenge). The slopes from the linear regions in part a) provide the apparent rate constants $k_p[P^-]$ which are plotted as a function of $f_{AN,0}$ in Figure 23.



Figure 23: Apparent rate constants $\langle k_p \rangle [P \cdot]$ (where $\langle k_p \rangle$ is the average propagation rate constant and [P[·]] is the concentration of propagating macroradicals) for styrene/acrylonitrile (S/AN) copolymerizations versus initial AN feed composition, $f_{AN,0}$, using NHS-BlocBuilder (•) at 115 °C in 50% 1,4-dioxane solution.

GPC analysis of samples taken during the polymerization indicated that in all cases, S/AN copolymers possessed narrow MWDs with low polydispersities ranging from 1.14-1.26 (Figure 23) and exhibited relatively linear M_n versus X plots (Figure 24). GPC was done in DMF using linear PMMA samples and thus corrections were again necessary using compositionally averaged Mark-Houwink coefficients^[110,112] in order to estimate the actual molecular weight of the copolymers. The plots are linear up to \approx 70% conversion ($M_n = 18.1 \text{ kg} \text{ mol}^{-1}$)

indicating a controlled polymerization is approached. The molecular weight characteristics and final copolymer compositions are summarized in Table 14.



Figure 24: Gel permeation chromatograms of samples taken at various times for S/AN copolymerizations (denoted by S-*ran*-AN) performed in 50 wt% 1,4dioxane solution at 115 °C with target molecular weights at complete conversion of 25 kg·mol⁻¹ and with different monomer feed concentrations using NHS-BlocBuilder initiator. The experiments are denoted as S/AN-NHSBB-XX, where XX represents the initial molar feed concentration of AN given by f_{AN} : (a) S/AN-NHSBB-13, $f_{AN,0} = 0.13$; (b) S/AN-NHSBB-30, $f_{AN,0} = 0.30$; (C) S/AN-NHSBB-

52, $f_{AN,0} = 0.52$; (d) S/AN-NHSBB-86, $f_{AN,0} = 0.86$. The GPC was performed in DMF at 50 °C using PMMA standards.



Figure 25: Number average molecular weight (M_n) versus conversion (X) for styrene/acrylonitrile (S/AN) copolymerizations performed in 50 wt% 1,4-dioxane solution at 115 °C with target molecular weights at complete conversion of 25 kg·mol⁻¹, using NHS-BlocBuilder at various AN initial molar feed compositions, $f_{AN,0} = 0.13$ (\diamondsuit), 0.20 (\bigtriangleup), 0.30 (\Box), 0.39 (\bigcirc) and 0.52 (\blacklozenge), 0.70 (\blacktriangle) and 0.86 (\blacksquare).

Similarly to the S/AN-BB copolymers, the final molar composition of AN found by FTIR shows that at low $f_{AN,0}$, the molar composition of AN was significantly richer than that of the feed, while at high $f_{AN,0}$ ($f_{AN,0} > 0.50$) the copolymer composition became increasingly less rich in AN compared to the feed. In experiment ID S/AN-NHSBB-52, S/AN-NHSBB-70 and S/AN-NHSBB-86 (displayed in Table 14, with $f_{AN,0} = 0.52$, 0.70 and 0.86, respectively), AN molar compositions, F_{AN} , of only 0.46, 0.50 and 0.52 resulted in the copolymers. As the suggested range of AN (F_{AN}) to reduce O₂ and CO₂ permeability in the S/AN copolymer is between 0.40 to 0.66 (25-50 wt% AN)^[79], $f_{AN,0} > \approx 30$ mol% should be used to obtain an AN content in the S/AN copolymer for effectively reducing permeability of these organic compounds.

3.3.3 tert-Butyl Methacrylate/Acrylonitrile Random Copolymers (poly(t-BMA/AN)) using 8mol% SG1 relative to BlocBuilder Initiator

Prior to synthesizing S/AN copolymers with COOH functionality at random locations along the chain length for coupling with epoxy functional PE, it was necessary to understand how the copolymer feed composition controls the reactivity and kinetics in each of the following binary systems: S/AN, *t*-BMA/S and *t*-BMA/AN copolymers. The *t*-BMA incorporated into the copolymer could have the protecting group, leaving the acid that could be used later in melt-blending with epoxy-functional polyolefin resins. The results would be useful for subsequent tailoring of compositions of copolymers were successfully synthesized as described in Sections 3.3.1 and 3.3.2. *t*-BMA/S copolymers have been studied and reported by our research group^[75] at the same conditions described in our study here. *t*-BMA/S mixtures ranging from 10-92 mol% *t*-BMA in the feed were successfully synthesized using 10 mol% SG1 relative to BlocBuilder initiator at 90°C with target molecular weight of 25 kg·mol⁻¹.

copolymers exhibited monomodal MWDs, low polydispersities ($M_w/M_n < 1.30$) and relatively linear behaviour M_n up to about 40 mol% conversion.

t-BMA/AN copolymers were synthesized using BlocBuilder initiator with an excess of SG1 (8.1-8.5 mol% SG1 relative to BlocBuilder) for AN feed compositions ranging from 11-80 mol%. The polymerizations were done in a 50 wt% 1,4-dioxane solution at 90°C with target molecular weight of 25 kg·mol⁻¹. Figure 26 shows the first-order kinetic plots of $ln(1-X)^{-1}$ versus time for t-BMA/AN copolymerizations. For all plots, conversion increased with a relatively linear trend up to \approx 50% scaled conversion (depending on the AN feed composition), implying a constant radical concentration and thus a controlled polymerization. Extraction of the apparent rate constants, $\langle k_p \rangle [P \cdot]$, from the slopes indicated that increasing AN feed concentration tended to decrease the polymerization rate from $(3.3 \pm 0.5) \times 10^{-5}$ to $(5.1 \pm 0.3) \times 10^{-6}$ s⁻¹. In the case using excess SG1 nitroxide, the $\langle k_p \rangle [P \cdot]$ values can be translated into $\langle k_p \rangle \langle K \rangle$ values as described in Section 3.1 of Chapter 2, which combines the two key features controlling the NMP process. $\langle k_p \rangle \langle K \rangle$ can be written as Equation 12 assuming: 1) [SG1] is added at sufficiently high concentration that it does not vary much during the course of polymerization so that $[SG1] \approx [SG1]_0$ (initial SG1 concentration) and 2) [P-SG1] \approx [BlocBuilder]₀ if the chains remain relatively pseudo-living, which holds approximately true early on in the polymerization (where $ln(1-X)^{-1}$ versus time plots were linear). This is verified by linear M_n versus X plots (Figure 29) for the copolymerizations in the composition ranges studied.

$$\langle k_{P} \rangle \langle K \rangle = \langle k_{P} \rangle \frac{[P \cdot][SG1]}{[P - SG1]} \approx = \langle k_{P} \rangle \frac{[P \cdot][SG1]_{0}}{[BlocBuilder]_{0}} \approx = \langle k_{P} \rangle [P \cdot]r$$
(12)

of $\langle k_p \rangle \langle K \rangle$ for t-BMA/AN experimental estimates The copolymerizations, plotted as a function of $f_{AN,0}$ in Figure 27, drop sharply with increasing AN content in the feed. The recently reported homo-propagation rate constant for AN ($k_{p,AN} = 1.1 \text{ x}10^4 \text{ L mol}^{-1} \text{ s}^{-1[114]}$) is between half to one order magnitude higher compared to the homopropagation rate constant of t-BMA ($k_{p,t}$ - $_{BMA} = 1.6 \times 10^3 \text{ L mol}^{-1} \text{ s}^{-1[121]}$) at 90°C. However, there is a larger discrepancy between the equilibrium constant K of AN and t-BMA. As noted previously, Nicolas et al. took $K_{AN} \approx K_{BA} = 1 \times 10^{-11} \text{ mol } L^{-1}$, while the equilibrium constant for *t*-BMA was approximated to be structurally similar to MMA, thus K_t $_{BMA} \approx K_{MMA} = 2.6 \text{ x } 10^{-7} \text{ mol } \text{L}^{-1}$. As data for the *t*-BMA/AN copolymerization is limited and the only reactivity ratios known for the particular system are those derived from our study (provided in Section 3.3.5), a terminal model was used to describe the kinetics for this system. The expression derived by Charleux et al. for such a model was compared against our experimental data:^[23]

$$\left\langle k_{p} \right\rangle \left\langle K \right\rangle = \frac{r_{AN}f_{AN}^{2} + 2f_{AN}f_{t-BMA} + r_{t-BMA}f_{t-BMA}^{2}}{r_{AN}\frac{f_{AN}}{k_{p,AN}K_{AN}} + r_{t-BMA}\frac{f_{t-BMA}}{k_{p,t-BMA}K_{t-BMA}}}$$
(13)

From Figure 27, there is a reasonable agreement between the experimental data and the predicted $\langle k_p \rangle \langle K \rangle$ in the feed composition range studied. Additional testing of the model at lower AN feed compositions (with a large increase in $\langle k_p \rangle \langle K \rangle$ expected) would be useful; although a high AN feed composition is of interest for this study in order to improve barrier properties.



Figure 26: Kinetic plots of *t*-BMA/AN copolymerizations with BlocBuilder/SG1 (r = 8.1-8.5 mol%) at 90 °C in 50 wt% 1,4-dioxane as a function of AN molar feed composition, $f_{AN,0}$: $f_{AN,0} = 0.11$ (\diamondsuit), 0.30 (\blacksquare), 0.51 (\blacktriangle), 0.70 (\bigcirc) and 0.80 (\bigcirc). The slopes from the linear regions provide the apparent rate constants $k_p[P^{-}]$ (where k_p is the propagation rate constant and [P⁻] is the concentration of propagating radicals).



Figure 27: Product of average propagation rate with average equilibrium constant, $\langle k_p \rangle \langle K \rangle$ for poly(*t*-BMA/AN) copolymerizations versus initial AN feed composition, $f_{AN,0}$, using BlocBuilder/SG1 (•) at 90 °C in 50% 1,4-dioxane solution. The dashed line indicates the predicted terminal model for $\langle k_p \rangle \langle K \rangle^{[23]}$.

The molecular weight characteristics were determined by GPC relative to linear PS standards in THF solvent at 40°C. It should be noted that since the highest AN incorporated was 37 mol% in the final copolymer (Experiment ID: *t*-BMA/AN-BB/SG1-80 in Table 15, the samples were easily soluble in THF. The results were converted to the corresponding copolymer M_n based on the initial feed composition and the Mark-Houwink coefficients provided in the '*Characterization*' section (Section 3.2.5).^[110-112] Note that since the Mark-Houwink parameters used for poly(AN) were not in THF, the corrections may not

necessarily be perfect. GPC analysis for *t*-BMA/AN experiments resulted in monomodal MWDs with relatively low M_w/M_n (1.17-1.40) that are suggestive of a controlled polymerization. The GPC traces shown in Figure 28 display a leftward shift in MWD, indicating a steady, monomodal growth in the copolymer chains over time; although, chain extension experiments or determination of the end group concentration of SG1 would be definitive of a controlled polymerization. M_n versus X plots (Figure 28) are linear up to ≈ 55 % conversion ($M_n = 14.8$ kg mol⁻¹) for the different AN feed compositions, indicating that a true "living" polymerization is approached. In some cases, the M_n s begin to slightly plateau at high conversions indicating some irreversible termination reactions may be occurring. The molecular weight characteristics and final copolymer compositions are summarized in Table 15.



Figure 28: Gel permeation chromatograms of samples taken at various times for *t*-BMA/AN copolymerizations performed in 50 wt% 1,4-dioxane at 90 °C with $M_{n,target}$ at complete conversion of 25 kg·mol⁻¹ and with different monomer feed concentrations using BlocBuilder/SG1 initiator. The experiments are denoted as *t*-

BMA/AN-BB/SG1-XX, where XX represents the initial molar feed concentration of AN given by f_{AN} : (a) *t*-BMA/AN-BB/SG1-11, $f_{AN,0} = 0.11$; (b) *t*-BMA/AN-BB/SG1-30, $f_{AN,0} = 0.30$. The GPC was performed in THF at 40 °C using PS standards.



Figure 29: Number average molecular weight (M_n) versus conversion (X) for *tert*butyl methacrylate/acrylonitrile (*t*-BMA/AN) copolymerizations performed in 50 wt% 1,4-dioxane solution at 90 °C with target molecular weights at complete conversion of 25 kg·mol⁻¹ using BlocBuilder/SG1 at various AN feed concentrations: $f_{AN,0} = 0.11$ (\diamondsuit), 0.30 (\blacksquare), 0.51 (\blacktriangle) and 0.70 (\bigcirc).

FTIR was used with poly(*t*-BMA) and poly(AN) standards to identify the copolymer compositions. It was more difficult to achieve a high AN content in the final *t*-BMA/AN copolymers compared to the S/AN copolymers. At low $f_{AN,0}$, the molar composition of AN was about equal to that of the feed, while for $f_{AN,0} > 0.30$, the copolymer composition became increasingly less rich in AN compared to the feed. For example, in experiment ID *t*-BMA/AN-BB/SG1-80 with $f_{AN,0} = 0.80$, only $F_{AN} = 0.37$ was incorporated in the final copolymer. This study

illustrates that it should be simple to randomly incorporate the acid functionality in S/AN using *t*-BMA, since a low acid concentration (< 10 mol%) would likely be sufficient for reactive blending with PE. Note that the *tert*-butyl group must be removed by mild acid treatment to yield the carboxylic acid prior to melt-blending with epoxy functional PE.

3.3.4 tert-Butyl Methacrylate/Acrylonitrile Random Copolymers (poly(t-BMA-ran-AN)) using NHS-BlocBuilder Initiator

NHS-BlocBuilder has been an efficient initiator for styrene and *n*-butyl acrylate polymerizations;^[68] consequently, we predict that the NHS-group can serve as a protecting group and that the NHS-BlocBuilder can sufficiently release enough SG1 from the start of the reaction to effectively control *t*-BMA-rich copolymerizations. The suitability of NHS-BlocBuilder for *t*-BMA/AN copolymerizations was studied with the same conditions as the former section (Section 3.3.3), but without any added free nitroxide. *t*-BMA/AN copolymerizations ($f_{AN,0} = 0.094-0.81$) synthesized in a 50 wt% 1,4-dioxane solution at 90°C with M_n at complete conversion of 25 kg·mol⁻¹, show that NHS-BlocBuilder could effectively control the polymerizations. In Figure 30, the semilogarithmic plots of $ln(1-X)^{-1}$ versus time for *t*-BMA/AN copolymerizations with $f_{AN,0}$ ranging from 0.094-0.81, show that conversion increased with a relatively linear trend up to $\approx 70\%$. Extraction of the apparent rate constants, $\langle k_p \rangle [P \cdot]$, from the slopes indicated that increasing AN feed concentration tended to decrease the

polymerization rate from $(4.8 \pm 0.4) \times 10^{-5}$ at $f_{AN,0} = 0.094$ to $(8.4 \pm 0.2) \times 10^{-6}$ s⁻¹ $f_{AN,0} = 0.81$ as shown in Figure 31. These values are slightly greater than those estimated for *t*-BMA/AN copolymerizations using BlocBuilder/SG1 (Section 3.3.1), but they are reasonable as the estimated range of $\langle k_p \rangle [P \cdot]$ values reflect the difference in k_p of AN and *t*-BMA from the data reported by Junkers et al.^[114] and Roberts et al.^[121] respectively, as well as the estimated *K* values ($K_{AN} = 1 \times 10^{-11} \text{ L} \text{ mol}^{-1} \text{ s}^{-1[116]}$ and $K_{t-BMA} = 2.6 \times 10^{-7} \text{ L} \text{ mol}^{-1} \text{ s}^{-1[75]}$) available from the literature. The combined parameter k_pK for AN and *t*-BMA available in the literature at 90°C are evaluated to be $(k_pK)_{AN} \approx 1.1 \times 10^{-7} \text{ s}^{-1}$ and $(k_pK)_{t-BMA} \approx 4.2 \times 10^{-4} \text{ s}^{-1}$. For MMA polymerizations controlled by AN with $f_{AN,0} = 0.088$ using BlocBuilder/SG1 at 90°C, $\langle k_p \rangle \langle K \rangle = 2.6 \times 10^{-6} \text{ s}^{-1}$,^[116] which shows how a small addition of AN to control a methacrylate-rich NMP process has a dramatic effect on the kinetics due to the very high *K* of the methacrylate^[122] compared to S or AN.



Figure 30: Kinetic plots of *tert*-butyl methacrylate/acrylonitrile (*t*-BMA/AN) copolymerizations with NHS-BlocBuilder at 90 °C in 50 wt% 1,4-dioxane as a function of AN molar feed composition: $f_{AN,0} = 0.094$ (O), 0.30 (\triangle), 0.52 (\blacklozenge), 0.72 (\Box) and 0.81 (\blacklozenge). The slopes from the linear regions provide the apparent rate constants $\langle k_p \rangle [P \cdot]$.



Figure 31: Apparent rate constants $\langle k_p \rangle [P \cdot]$ (where $\langle k_p \rangle$ is the average propagation rate constant and [P[·]] is the concentration of propagating macroradicals) for (*t*-BMA/AN) copolymerizations versus initial AN feed composition, $f_{AN,0}$, using NHS-BlocBuilder (\bullet) at 90 °C in 50% 1,4-dioxane solution.

The molecular weight characteristics were determined by GPC relative to linear poly(styrene) standards in THF solvent at 40°C, thus the results were converted to the corresponding copolymer M_n based on composition using Mark-Houwink parameters (Section 3.2.5).^[110-112] The corrections may not necessarily be perfect since the Mark-Houwink parameters used for poly(AN) were not in THF. It should be noted once again that since only up to \approx 35 mol% AN was incorporated

in the final copolymers (Experiment ID: *t*-BMA/AN-NHSBB-81 in Table 16), the samples were soluble in THF. GPC analysis of samples taken during the polymerization indicated in most cases, *t*-BMA/AN copolymers possessed narrow MWDs with M_w/M_n ranging from 1.23-1.50 (Figure 32) and exhibited relatively linear M_n versus conversion plots up to $\approx 60\%$ conversion (Figure 33, $M_n = 15.6$ kg mol⁻¹). In some cases, the M_n s begin to faintly plateau at very high conversions indicating some irreversible termination reactions started to occur. These results suggest NHS-BlocBuilder could be a successful controller for the methacrylaterich copolymerizations without additional SG1. Chain extension experiments would be useful to confirm the degree of "livingness" for the polymerizations, and 13C NMR would confirm that the protected methacrylic acid, *t*-BMA, minimized backbiting or chain transfer reactions, and degradation of the alkoxyamine.^[49,107] The final copolymer compositions and the molecular weight characteristics are summarized in Table 16.



Figure 32: Gel permeation chromatograms of samples taken at various times for *t*-BMA/AN copolymerizations performed in 50 wt% 1,4-dioxane solution at 90 °C with $M_{n,target}$ at complete conversion of 25 kg·mol⁻¹ and with different monomer feed concentrations using NHS-BlocBuilder initiator. The experiments are denoted as *t*-BMA/AN-NHSBB-XX, where XX represents the initial molar feed concentration of AN given by f_{AN} : (a) *t*-BMA/AN-NHSBB-10, $f_{AN,0} = 0.094$; (b) *t*-BMA/AN-NHSBB-52, $f_{AN,0} = 0.52$ (refer to Table 16). The GPC was performed in THF at 40 °C using PS standards.



Figure 33: Number average molecular weight (M_n) versus conversion (X) for *tert*butyl methacrylate/acrylonitrile (*t*-BMA/AN) copolymerizations performed in 50 wt% 1,4-dioxane solution at 90 °C with target molecular weights at complete conversion of 25 kg·mol⁻¹ using NHS-BlocBuilder at various AN feed concentrations, $f_{AN,0}$: $f_{AN,0}$ = 0.094 (\diamondsuit), 0.30 (\blacktriangle), 0.52 (\blacksquare), 0.72 (\times) and 0.81 (\bigcirc).

FTIR was used for the compositional analysis of the *t*-BMA/AN copolymers. At low $f_{AN,0}$ ($f_{AN,0} = 0.094$) the molar composition of AN was about equal to that of the feed, while for $f_{AN,0} > 0.30$, the copolymer composition became increasingly less rich in AN compared to the feed. For example, in experiment ID *t*-BMA/AN-

NHSBB-72 and *t*-BMA/AN-NHSBB-81 with $f_{AN,0} = 0.72$ and 0.81, respectively, only ($F_{AN} =$) 0.33 and 0.35 was incorporated in the final copolymer. As was mentioned in Section 2.3.3, since a low acid concentration (<10 mol%) would likely be sufficient for reactive blending with PE, acid functionality should be easily incorporated in S/AN at random locations along the chain via the intermediary *t*-BMA (to be treated with a mild acid to generate the carboxylic acid for coupling with epoxy). The results of the poly(S-*ran*-AN) and poly(t-BMA*ran*-AN) studies with both unimolecular initiators (BlocBuilder and NHS-BlocBuiler) led to the estimation of reactivity ratios which are described in Section 3.5.5.

3.3.5 Copolymer Composition

The copolymer composition with respect to monomer "1", F_1 , may be quite different from that of the feed composition f_1 . The copolymer composition can be obtained from well-known relationships such as the Mayo-Lewis^[84] equation (*Equation 14*) which requires the knowledge of the monomer reactivity ratios^[85,87,88] r_1 and r_2 that describe the preference of monomer "1" attaching to a chain with terminal unit of "1" relative to a terminal unit of "2" (r_1) and the preference of monomer "2" attaching to a chain with terminal unit of "2" relative to a terminal unit of "1" (r_2).

$$F_{1} = \frac{r_{1}f_{1}^{2} + f_{1}(1 - f_{1})}{r_{2}(1 - f_{1})^{2} + 2f_{1}(1 - f_{1}) + r_{1}f_{1}^{2}}$$
(14)

Tables 14 to 16 summarize the compositions for the copolymers synthesized from various initial feed compositions. The copolymer compositions were predicted in terms of the initial monomer concentrations using Mayo's^[84] terminal copolymerization model^[40,74] assuming the active site reactivity depends on the nature of the reactive terminus. Monomer reactivity ratios for S/AN and *t*-BMA/AN copolymerizations were determined from FTIR data via the Fineman-Ross^[85] and Kelen-Tüdös^[87,89] methods and by a nonlinear least-squares minimization fit (using MatLab with 95% confidence bound) to the Mayo-Lewis equation.

conventional radical polymerization, reactivity ratios For for S/AN copolymerizations are well known. Reactivity ratios may be slightly different for controlled radical polymerizations as the retardation of the termination processes results in chains with much higher chain-to-chain compositional homogeneity compared to conventional radical polymerizations. The effect of the initiator, whether it was BlocBuilder or NHS-BlocBuilder, was negligible at the temperature studied. The reactivity ratios for S/AN copolymerizations using BlocBuilder and NHS-BlocBuilder were $r_{AN} = 0.07 \pm 0.01$, 0.09 ± 0.01 and $r_S =$ 0.27 ± 0.02 , 0.39 ± 0.02 by the Finemann-Ross method and $r_{AN} = 0.10 \pm 0.01$, 0.11 ± 0.01 and $r_s = 0.28 \pm 0.02$, 0.42 ± 0.03 by the Kelen-Tüdös method. Conventional radical copolymerization of S/AN provided reactivity ratios of r_{AN} = 0.04-0.06 and $r_s = 0.47-0.54^{[124]}$. These reactivity ratios are summarized in the Mayo plots shown in Figure 34, which indicate the copolymer composition expected for a given feed. The Mayo plot implies that it was more difficult to obtain S/AN copolymer rich in AN as the feed concentration of AN was increased. The azeotropic composition at about 40 mol% AN suggests it is the most "efficient" feed to obtain a satisfactory incorporation of AN in the copolymer.



Figure 34: Mayo plot showing acrylonitrile composition (F_{AN}) versus acrylonitrile initial molar feed composition ($f_{AN,0}$) for S/AN copolymers with NHS-BlocBuilder at 115 °C in 1,4-dioxane.

The reactivity ratios for t-BMA/AN copolymerizations using BlocBuilder and NHS-BlocBuilder were $r_{AN} = 0.07 \pm 0.01$, 0.08 ± 0.01 and $r_{t-BMA} = 1.24 \pm 0.20$, 1.28 ± 0.15 by the Finemann-Ross method, and were $r_{AN} = 0.14 \pm 0.03$ (with both BlocBuilder and NHS-BlocBuilder) and $r_{t-BMA} = 0.89 \pm 0.19$, 0.95 ± 0.17 by the Kelen-Tüdös method. S/AN reactivity ratios were not provided in the literature, thus, isobutyl methacrylate (*i*-BMA)/AN reactivity ratios provided by Nair et al.

using conventional radical copolymerization were used as a comparison: $r_{AN} = 0.21$ and $r_{i-MMA} = 1.04$.^[125] The reactivity ratios are near those reported from our study, thus the related system would have a similar Mayo plot to that estimated for our *t*-BMA/AN system (shown in Figure 35). The Mayo plot implies that it was quite difficult to obtain *t*-BMA/AN copolymer rich in AN as the feed concentration of AN was increased.



Figure 35: Mayo plot showing acrylonitrile composition (F_{AN}) versus acrylonitrile initial molar feed composition ($f_{AN,0}$) for *t*-BMA/AN copolymers with BlocBuilder/SG1 at 90 °C in 1,4-dioxane.

3.3.6 tert-Butyl Methacrylate/Styrene/Acrylonitrile Random Terpolymer (poly(t-BMA-ran-S/AN)) using NHS-BlocBuilder Initiator

In order to achieve S/AN copolymers with COOH functionality at random locations along the chain length as depicted in Route B of Figure 16, a terpolymerization of S, AN and *t*-BMA was used. With a better understanding of the reactivity and kinetics for each binary system (S/*t*-BMA, S/AN and *t*-

BMA/AN), appropriate monomer feed concentrations were easily selected to produce S/AN with sufficient random carboxylic acid functionality (<10 mol%) (S-*ran*-AN-*ran*-COOH). A *t*-BMA/S/AN terpolymer was synthesized using NHS-BlocBuilder initiator in a 50 wt% 1,4-dioxane solution at 90°C with $M_{n,target}$ of 25 kg·mol⁻¹ and monomer feed composition in the mixture of $f_{AN,0} = 0.50$, $f_{S,0} = 0.40$ and $f_{t-BMA,0} = 0.10$. The first-order kinetic plot of $ln(1-X)^{-1}$ versus time (Figure 36) exhibited a relatively linear trend up to ≈ 54 % conversion.



Figure 36: Kinetic plot of *t*-BMA/S/AN terpolymerizations with NHS-BlocBuilder at 90 °C in 50 wt% 1,4-dioxane with a molar feed composition of $f_{AN,0} = 0.50, f_{S,0} = 0.40$ and $f_{t-BMA,0} = 0.10$.

The molecular weight characteristics were determined by GPC relative to linear PS standards in THF solvent at 40°C, thus the results were converted to the corresponding copolymer M_n based on compositionally averaged Mark-Houwink

coefficients (presented in Section 3.2.5).^[110-112] GPC analysis of samples taken during the polymerization indicated that in all cases, *t*-BMA/S/AN terpolymer possessed narrow MWDs with low polydispersities (between 1.10-1.19) (Figure 37) and exhibited a linear M_n versus X plot up to about 54 % conversion (Figure 38, $M_n = 13.6$ kg mol⁻¹). Thus, NHS-BlocBuilder appears to be an effective controller for *t*-BMA/S/AN terpolymerization without any added free nitroxide, which is not necessarily surprising as the composition is comparatively rich in S and AN. The molecular weight characteristics and final copolymer compositions are summarized in Table 17.



Figure 37: Gel permeation chromatograms of samples taken at various times for *t*-BMA/S/AN terpolymerization performed in 50 wt% 1,4-dioxane solution at 90 °C with $M_{n,target}$ at complete conversion of 25 kg·mol⁻¹ using NHS-BlocBuilder initiator. The experiment is denoted as *t*-BMA/S/AN-NHSBB-10/50, which refers to *t*-BMA/S/AN terpolymerization done with NHS-BlocBuilder where 10 is the molar feed composition with respect to *t*-BMA and 50 is the molar feed composition with respect to AN. The GPC was performed in tetrahydrofuran

(THF) at 40 °C using PS standards.



Figure 38: Number average molecular weight (M_n) versus conversion (X) for *t*-BMA/S/AN) terpolymerization performed with target molecular weights at complete conversion of 25 kg·mol⁻¹ using NHS-BlocBuilder at 90 °C with monomer feed concentration of: $f_{AN,0} = 0.50$, $f_{S,0} = 0.40$ and $f_{t-BMA,0} = 0.10$.

The final molar composition for the *t*-BMA/S/AN terpolymer, determined using FTIR, was $F_{t-BMA} = 0.11$, $F_S = 0.42$ and $F_{AN} = 0.47$, which is very close to the feed composition. With the sufficient concentration of the acid precursor and AN that both randomly incorporated in the terpolymer (F_{AN} between 0.40 to 0.66 is recommended in S/AN copolymers to improve its barrier properties (Figure 15, 25-50 wt% AN)), a suitable terpolymer is now available for future reactive blending experiments with epoxy-functional PE.

3.4 Conclusion

The suite of functional S/AN resins ($f_{AN} = 0.10-0.86$) was completed with controlled placement of the acid or amino-precursor groups at one chain end. The incorporation of AN into styrenic resins has been possible at relatively high loadings, in some cases up to $\approx 52 \text{ mol}\%$ AN using either BlocBuilder or NHS-BlocBuilder, which should provide excellent barrier properties once blended into the appropriately functionalized PE. The S/AN resins were synthesized in a controlled manner with narrow molecular weight distribution $(M_w/M_n = 1.14$ -1.26) and relatively linear M_n versus conversion plots ($M_n = 15.3-18.1 \text{ kg mol}^{-1}$, X = 40-70%), suggesting the ability for such resins to serve as macroinitiators for addition of a second block. They may also be sufficient on their own as functional polymers for blending (the BlocBuilder initiated S/AN resins would be as useful as carboxylic acid terminated resins for reactive blending with epoxy functional PE while the NHS-terminated S/AN can be converted into a primary amine terminated S/AN that can be blended with maleated PE). AN containing resins with random carboxylic acid functionality were derived by using the protected form of methacrylic acid, t-BMA, thus the binary t-BMA/AN system was studied. For $f_{AN} = 0.10-0.80$, the *t*-BMA/AN copolymers were relatively controlled with relatively narrow molecular weight distribution ($M_w/M_n = 1.17$ -1.50) and relatively linear M_n versus conversion plots ($M_n = 14.8-15.6$ kg mol⁻¹, X = 55-60%) using both BlocBuilder and NHS-BlocBuilder. The reactivity ratios were $r_{AN} = 0.07 \pm 0.01$ to 0.11 ± 0.01 , $r_S = 0.27 \pm 0.02$ to 0.42 ± 0.03 for S/AN

copolymerizations and $r_{AN} = 0.07 \pm 0.01$ to 0.14 \pm 0.03, $r_{t-BMA} = 0.89 \pm 0.19$ to 1.28 \pm 0.15 for *t*-BMA/AN copolymerizations. The reactivity ratios did not differ significantly when using BlocBuilder or NHS-BlocBuilder initiator for both binary systems, and were in agreement with previous literature for conventional radical polymerization. After examining the binary systems, the *t*-BMA/S/AN terpolymer synthesis at a desirable composition for sufficient acid functionality and AN concentration was targeted, resulting in a terpolymer with $F_{AN} = 0.47$, $F_{S} = 0.42$, $F_{t-BMA} = 0.11$, nearly equal to the feed content. The terpolymer possessed a narrow molecular weight distribution ($M_w/M_n = 1.19$) and a fairly linear increase in M_n up to roughly 54% conversion. The AN containing copolymers and terpolymers showed that BlocBuilder and NHS-BlocBuilder have the ability to control a wide range of resins for future designs of tailored AN-containing resins attractive for barrier applications.

4.0 General Conclusions

The copolymerization of a protected styrenesulfonate by NMP was effective in producing well-defined copolymers as templates for membrane applications. Additionally, acrylonitrile was incorporated into resins at relatively high loadings by NMP, producing well-defined copolymers as templates for barrier applications.

As a route towards obtaining amphiphilic precursors for separations membranes, poly(SS-TOA) and poly(SS-TOA-*ran*-S) were synthesized at 90-

110°C in toluene using 8.5 mol% SG1 relative to BlocBuilder. The polymers were more controlled for lower target molecular weight systems and in some cases, resulted in M_w/M_n as low as 1.02 and a linear increase in M_n with conversion up to about 35%. The reported $\langle k_p \rangle \langle K \rangle$ values of SS-TOA were ~1.5-2 times greater than styrene homopolymerizations at the same temperature. Reactivity ratios for poly(SS-TOA-*ran*-S) were $r_{SS-TOA} = 4.43 \pm 0.16$ to 6.49 ± 0.06 and $r_{Styrene} = 0.74 \pm$ 0.03 to 1.10 ± 0.10, signifying comparatively richer SS-TOA for a given feed. Similarly to styrene, SS-TOA was determined to be an effective controlling comonomer for BlocBuilder-mediated NMP through the synthesis of poly(SS-TOA*grad*-GMA). The prepared sulfonated polymers and copolymers as amphiphilic precursors indicate NMP is a possible synthetic route towards achieving such materials for a number of applications such as templates for membranes.

As a route to developing barrier materials, S/AN random copolymers were synthesized at 90°C in 1,4-dioxane with controlled placement of functional groups at one chain end using BlocBuilder and NHS-BlocBuilder initiators. Narrow molecular weight distributions ($M_w/M_n = 1.14-1.26$) and relatively linear M_n up to about 70% conversion were found, suggesting effectively controlled polymerizations. Adequate amounts of AN were incorporated into the styrenic resins (up to 52 mol% AN) to be suitable as a barrier to organic contaminants. *t*-BMA/AN random copolymers were also synthesized at 90°C in 1,4-dioxane using BlocBuilder (with 10 mol% SG1 relative to BlocBuilder) and NHS-BlocBuilder initiators, both providing good control of the polymerizations. The *t*-BMA/AN

copolymers displayed relatively narrow molecular weight distributions (M_w/M_n = 1.17-1.50) and relatively linear M_n up to about 60% conversion in some cases, using both BlocBuilder and NHS-BlocBuilder. Estimated reactivity ratios for poly(S-ran-AN) were $r_{AN} = 0.07 \pm 0.01$ to 0.11 ± 0.01 and $r_S = 0.27 \pm 0.02$ to 0.42 \pm 0.03, and for poly(*t*-BMA-*ran*-AN) were $r_{AN} = 0.07 \pm 0.01$ to 0.14 \pm 0.03 and r_{t} . $_{BMA} = 0.89 \pm 0.19$ to 1.28 ± 0.15 using BlocBuilder or NHS-BlocBuilder. The two initiators did not affect the estimated reactivity ratios. The values were found to be in agreement with previous literature for conventional radical polymerization. Lastly, a *t*-BMA/S/AN terpolymer was produced (same conditions as the binary systems using NHS-BlocBuilder) with a low polydispersity ($M_w/M_n = 1.19$), narrow molecular weight distribution and linear M_n until ≈ 54 % conversion, to yield S/AN with COOH functionality at random locations along the chain. The ability of BlocBuilder and NHS-BlocBuilder to control a wide range of resins was revealed through AN containing copolymers and terpolymers, which act as an initial phase for designing more sophisticated resins for AN-copolymer barrier materials. The overall study recognizes NMP as a possible synthetic route towards achieving well-defined materials that could eventually be targeted as templates for membrane and barrier applications

Future Work

The recently developed NHS-BlocBuilder unimolecular initiator (shown to control styrene, n-butyl acrylate, glycidyl methacrylate and *tert*-butyl

methacrylate) could be used as a macroinitiator for the ring opening polymerization of lactide to form block copolymers due to the versatile terminal NHS group. Thus, it can be used for post-polymerization transformations of NHS with simplified formulations, as it possibly eliminates the need for excess SG1. NHS-BlocBuilder terminated poly(SS-TOA-*grad*-GMA) contains the functional segment and tough matrix material desired for nanoporous templates, as described in Section 2.1; it would be interesting to focus on the incorporation of a sacrificial segment that is selectively degradable. In this way, ABC triblock copolymers would be prepared with the diverse morphologies to serve as templates for nanoporous membranes. It would also be interesting to examine the copolymers' cross-linking ability of the epoxy groups inherent in GMA, a desirable feature for nanoporous membranes.^[126]

Much work remains towards developing the new S/AN-based barrier materials. The acid functional S/AN resins can be melt-blended with commercially available epoxy functional PE to form a block copolymer at the interface. In order to perform melt-blending experiments of the *t*-BMA/S/AN terpolymers, the *tert*-butyl protecting group must first be removed. A mild acid treatment can provide the carboxylic acid needed to react with the epoxy functional PE. For reactive blending of the amino-precursor S/AN resins (NHS-BlocBuilder terminated) with anhydride functional PE, the copolymers must first be converted into a primary amine terminated S/AN. This can be realized by reaction of NHS-BlocBuilder initiated poly(S-*ran*-AN) with excess diamine (Figure 39), as shown by Vinas et

al. for NHS-BlocBuilder initiated poly(styrene) by post-polymerization with ethanolamine yielding an OH functional poly(styrene) in their case.^[68] Reactive polymer blending can provide the stabilized morphologies desired for barrier applications, but the use of flow in combination with morphological stabilization can more favourably orient the domains. Many barrier materials consist of elongated domains dispersed within the matrix, as is the case for PE blends with lamellar nylon domains.^[99,127] Blends from the extruder can be placed in a channel die to create and orient the elongated domains by applying heat and pressure. Following extrusion and orientation, microscopy can be used to study transformations in morphology and to relate the findings to rheological properties. The stability of the S/AN/PE blends could then be examined by performing annealing experiments. These results would eventually lead to blend formulations for scale-up to more extensively test the S/AN-based materials to determine whether they could serve as a barrier against organic contaminants (specifically O_2 and CO_2 permeability).



NHS-BlocBuilder

Poly(styrene-ran-acrylonitrile)-NH2

Figure 39: Procedure to produce amine-end functional styrene/acrylonitrile (S/AN) resins by first using NHS-BlocBuilder to initiate S/AN copolymerizations followed by a recovery step and then reaction with a diamine to yield the amine terminated polymer.

5.0 Appendix

5.1 Figure Captions

Figure 1: Block copolymer microstructures for AB diblock polymeric system^[7]

Figure 2: Preparation of nanoporous nonoliths from triblock copolymer precursors.^[1]

Figure 3: Structures of initiators: a) TEMPO, b) SG1 (free nitroxide) and c) BlocBuilder (unimolecular initiator).

Figure 4: Synthesis of (a) Trioctylammonium p-styrenesulfonate (SS-TOA) Monomer (b) trioctylammonium p-styrenesulfonate Homopolymers (poly(SS-TOA)) and (c) Trioctylammonium p-styrenesulfonate/Styrene random Copolymers (poly(SS-TOA-*ran*-S)).

Figure 5: Semilogarithmic plot of $ln(1-X)^{-1}$ (where X = conversion) versus time for homopolymerizations of trioctylammonium p-styrenesulfonate (SS-TOA) at various temperatures for two target molecular weights using 8.5 mol% SG1 free nitroxide relative to BlocBuilder. The various temperatures are represented symbolically by: (•) 90°C, (\diamond) 95°C, (•) 100°C, (\triangle) 105°C. Filled symbols denote M_n versus X for homopolymerizations with a target molecular weight of 20 kg·mol⁻¹ (---), while open symbols denote M_n versus X for homopolymerizations with a target molecular weight of 45 kg·mol⁻¹ (- - -). Note the plots do not always pass 0. The time for the start of the reaction was taken once the desired temperature was reached, but polymer may have formed as a high temperature (> 80°C) was approached.

Figure 6: Trioctylammonium p-styrenesulfonate homopolymerization (SS-TOA-100) at 100°C with target molecular weight of 20 kg·mol⁻¹ using 8.5 mol% SG1 free nitroxide relative to BlocBuilder

Figure 7: Number-average molecular weight (M_n) versus conversion (X) for trioctylammonium p-styrenesulfonate homopolymerizations at various temperatures for two target molecular weights using 8.5 mol% SG1 free nitroxide relative to BlocBuilder. The various temperatures are represented symbolically by: (\bullet) 90°C, (\diamond) 95°C, (\blacksquare)

100°C, (\triangle) 105°C. Filled symbols denote M_n versus X for homopolymerizations with a target molecular weight of 20 kg·mol⁻¹ (----), while open symbols denote M_n versus X for homopolymerizations with a target molecular weight of 45 kg·mol⁻¹ (----).

Figure 8: Polydispersity index (M_w/M_n) versus conversion (X) for trioctylammonium pstyrenesulfonate homopolymerizations at various temperatures for two target molecular weights using 8.5 mol% SG1 free nitroxide relative to BlocBuilder. The various temperatures are represented symbolically by: (•) 90°C, (\diamond) 95°C, (\blacksquare) 100°C, (\triangle) 105°C. Filled symbols denote M_w/M_n versus X for homopolymerizations with a target molecular weight of 20 kg·mol⁻¹ (---), while open symbols denote M_w/M_n versus X for homopolymerizations with a target molecular weight of 45 kg·mol⁻¹ (---).

Figure 9: Gel permeation chromatograms of samples taken at various times for SS-TOA/S copolymerizations poly(SS-TOA-*ran*-S) performed at 110°C in toluene with theoretical molecular weights at complete conversion of 30 kg·mol⁻¹ and with different monomer feed concentrations (initial molar feed concentration of SS-TOA is given by $f_{SS-TOA,0}$) using SG1/BlocBuilder initiator: (a) SS-TOA/S-20/80: $f_{SS-TOA,0} = 0.23$; (b) SS-TOA/S-40/60: $f_{SS-TOA,0} = 0.43$; (C) SS-TOA/S-50/50: $f_{SS-TOA,0} = 0.50$; (d) SS-TOA/S-60/20: $f_{SS-TOA,0} = 0.63$. Refer to Table 5 for complete information. All GPC samples were prepared by dissolving in solvent system of 2wt% TOA in THF.

Figure 10: Mayo-Lewis plot of copolymer composition with respect to *SS-TOA*, F_{SS-TOA} , versus monomer feed composition, $f_{SS-TOA,0}$, using *SS-TOA* and styrene reactivity ratios determined from Fineman-Ross and Kelen-Tüdös methods and from nonlinear least-squares fitting of the Mayo-Lewis equation to the experimental data ($r_{SS-TOA} = 4.43$ to 6.49 and $r_{Styrene} = 0.74$ to 1.10). The fits are indicated by the dashed lines while the experimental data for copolymerizations done in toluene at 110 °C using BlocBuilder as the unimolecular initiator and 8.5 mol % free nitroxide SG1 relative to BlocBuilder is indicated by the solid circles. The straight line indicates the azeotropic composition ($f_{SS-TOA} = F_{SS-TOA}$).

Figure 11: Gel permeation chromatogram of samples taken just before addition of glycidyl methacrylate (GMA) to SS-TOA (at 220 min) denoted by (-----) and at a later time (at 400 min) denoted by (----) for gradient polymerization at 90°C using poly(SS-105

TOA) as macroinitiator ($X_{SS-TOA} = 25\%$) to polymerize with GMA.

Figure 12: Reactive polymer blending for compatibilizing polymer blends

Figure 13: Reactions between (top) a cyclic anhydride and a 1° amine to first yield amic acid, and after condensation, an imide and between (bottom) carboxylic acid and epoxy groups to yield an ester.

Figure 14: Structure of a) BlocBuilder and b) SG1

Figure 15: O₂ and CO₂ permeability in the S/AN copolymer as a function of acrylonitrile (AN) content.^[79]

Figure 16: Routes for carboxylic acid functional styrene-*ran*-acrylonitrile (S/AN) copolymers using nitroxide-mediated polymerization (NMP) with BlocBuilder.

Figure 17: a) Synthetic scheme to convert the carboxylic acid functional BlocBuilder initiator into the protected *N*-succinimidyl ester form. b) styrene-*ran*-acrylonitrile (S/AN) copolymers using nitroxide-mediated polymerization (NMP) with NHS-BlocBuilder; the route towards producing single amine terminated S/AN upon reaction with excess diamine.

Figure 18: Kinetic plots of styrene/acrylonitrile (S/AN) copolymerizations with BlocBuilder at 90 °C in 50 wt% 1,4-dioxane as a function of molar feed composition of AN: $f_{AN,0} = 0.10 \ (\Box), 0.30 \ (\triangle), 0.40 \ (\diamondsuit), 0.50 \ (\blacksquare)$ and 0.70 (•). The slopes from the linear regions provide the apparent rate constants $k_p[P^{-}]$ which are plotted as a function of $f_{AN,0}$ in Figure 19

Figure 19: Apparent rate constants $\langle k_p \rangle [P \cdot]$ (where $\langle k_p \rangle$ is the average propagation rate constant and [P⁻] is the concentration of propagating macroradicals) for styrene/acrylonitrile (S/AN) copolymerizations versus initial AN feed composition, $f_{AN,0}$, using BlocBuilder (\bullet) at 90 °C in 50% 1,4-dioxane solution.

Figure 20: Gel permeation chromatograms of samples taken at various times for S/AN copolymerizations (denoted by S-*ran*-AN) performed in 50 wt% 1,4-dioxane solution at 90 °C with target molecular weights at complete conversion of 25 kg·mol⁻¹ and with 106

different monomer feed concentrations using BlocBuilder initiator. The experiments are denoted as S/AN-BB-XX, where XX represents the initial molar feed concentration of AN given by f_{AN} : (a) S/AN-BB-10, $f_{AN,0} = 0.10$; (b) S/AN-BB-30, $f_{AN,0} = 0.30$; (C) S/AN-BB-50, $f_{AN,0} = 0.50$; (d) S/AN-BB-70, $f_{AN,0} = 0.70$. The GPC was performed in DMF at 50 °C using PMMA standards.

Figure 21: Number average molecular weight (M_n) versus conversion (X) for styrene/acrylonitrile (S/AN) copolymerizations performed in 50 wt% 1,4-dioxane solution at 90 °C with target molecular weights at complete conversion of 25 kg·mol⁻¹, using BlocBuilder with various AN molar feed compositions: $f_{AN,0} = 0.10 \ (\Box), 0.30 \ (\triangle), 0.40 \ (\diamondsuit), 0.50 \ (\blacksquare)$ and 0.70 (\bullet) .

Figure 22: Kinetic plots of styrene/acrylonitrile (S/AN) copolymerizations with NHS-BlocBuilder at 115 °C in 50 wt% 1,4-dioxane solution for AN molar feed compositions: $f_{AN,0} = 0.13 \ (\Box), 0.20 \ (O), 0.30 \ (\triangle), 0.39 \ (\diamondsuit), 0.52 \ (\blacksquare), 0.70 \ (\bullet) and 0.86 \ (\diamondsuit).$ The slopes from the linear regions in part a) provide the apparent rate constants $k_p[P]$ which are plotted as a function of $f_{AN,0}$ in Figure 23.

Figure 23: Apparent rate constants $\langle k_p \rangle [P \cdot]$ (where $\langle k_p \rangle$ is the average propagation rate constant and [P[·]] is the concentration of propagating macroradicals) for styrene/acrylonitrile (S/AN) copolymerizations versus initial AN feed composition, $f_{AN,0}$, using NHS-BlocBuilder (\bullet) at 115 °C in 50% 1,4-dioxane solution.

Figure 24: Gel permeation chromatograms of samples taken at various times for S/AN copolymerizations (denoted by S-*ran*-AN) performed in 50 wt% 1,4-dioxane solution at 115 °C with target molecular weights at complete conversion of 25 kg·mol⁻¹ and with different monomer feed concentrations using NHS-BlocBuilder initiator. The experiments are denoted as S/AN-NHSBB-XX, where XX represents the initial molar feed concentration of AN given by f_{AN} : (a) S/AN-NHSBB-13, $f_{AN,0} = 0.13$; (b) S/AN-NHSBB-30, $f_{AN,0} = 0.30$; (C) S/AN-NHSBB-52, $f_{AN,0} = 0.52$; (d) S/AN-NHSBB-86, $f_{AN,0} = 0.86$. The GPC was performed in DMF at 50 °C using PMMA standards.

Figure 25: Number average molecular weight (M_n) versus conversion (X) for styrene/acrylonitrile (S/AN) copolymerizations performed in 50 wt% 1,4-dioxane
solution at 115 °C with target molecular weights at complete conversion of 25 kg·mol⁻¹, using NHS-BlocBuilder at various AN initial molar feed compositions, $f_{AN,0} = 0.13$ (\diamondsuit), 0.20 (\bigtriangleup), 0.30 (\Box), 0.39 (\bigcirc) and 0.52 (\blacklozenge), 0.70 (\blacktriangle) and 0.86 (\blacksquare).

Figure 26: Kinetic plots of *t*-BMA/AN copolymerizations with BlocBuilder/SG1 (r = 8.1-8.5 mol%) at 90 °C in 50 wt% 1,4-dioxane as a function of AN molar feed composition, $f_{AN,0}: f_{AN,0} = 0.11$ (\diamondsuit), 0.30 (\blacksquare), 0.51 (\blacktriangle), 0.70 (O) and 0.80 (\bigcirc). The slopes from the linear regions provide the apparent rate constants $k_p[P]$ (where k_p is the propagation rate constant and [P] is the concentration of propagating radicals).

Figure 27: Product of average propagation rate with average equilibrium constant, $\langle k_p \rangle \langle K \rangle$ for poly(*t*-BMA/AN) copolymerizations versus initial AN feed composition, $f_{AN,0}$, using BlocBuilder/SG1 (•) at 90 °C in 50% 1,4-dioxane solution. The dashed line indicates the predicted terminal model for $\langle k_p \rangle \langle K \rangle^{[23]}$.

Figure 28: Gel permeation chromatograms of samples taken at various times for *t*-BMA/AN copolymerizations performed in 50 wt% 1,4-dioxane at 90 °C with $M_{n,target}$ at complete conversion of 25 kg·mol⁻¹ and with different monomer feed concentrations using BlocBuilder/SG1 initiator. The experiments are denoted as *t*-BMA/AN-BB/SG1-XX, where XX represents the initial molar feed concentration of AN given by f_{AN} : (a) *t*-BMA/AN-BB/SG1-11, $f_{AN,0} = 0.11$; (b) *t*-BMA/AN-BB/SG1-30, $f_{AN,0} = 0.30$. The GPC was performed in THF at 40 °C using PS standards.

Figure 29: Number average molecular weight (M_n) versus conversion (X) for *tert*-butyl methacrylate/acrylonitrile (*t*-BMA/AN) copolymerizations performed in 50 wt% 1,4-dioxane solution at 90 °C with target molecular weights at complete conversion of 25 kg·mol⁻¹ using BlocBuilder/SG1 at various AN feed concentrations: $f_{AN,0} = 0.11$ (\diamondsuit), 0.30 (\blacksquare), 0.51 (\blacktriangle) and 0.70 (\bigcirc).

Figure 30: Kinetic plots of *tert*-butyl methacrylate/acrylonitrile (*t*-BMA/AN) copolymerizations with NHS-BlocBuilder at 90 °C in 50 wt% 1,4-dioxane as a function of AN molar feed composition: $f_{AN,0} = 0.094$ (O), 0.30 (\triangle), 0.52 (\blacklozenge), 0.72 (\Box) and 0.81 (\blacklozenge). The slopes from the linear regions provide the apparent rate constants $\langle k_p \rangle [P \cdot]$.

Figure 31: Apparent rate constants $\langle k_p \rangle [P \cdot]$ (where $\langle k_p \rangle$ is the average propagation rate constant and [P[·]] is the concentration of propagating macroradicals) for (*t*-BMA/AN) copolymerizations versus initial AN feed composition, $f_{AN,0}$, using NHS-BlocBuilder (•) at 90 °C in 50% 1,4-dioxane solution.

Figure 32: Gel permeation chromatograms of samples taken at various times for *t*-BMA/AN copolymerizations performed in 50 wt% 1,4-dioxane solution at 90 °C with $M_{n,target}$ at complete conversion of 25 kg·mol⁻¹ and with different monomer feed concentrations using NHS-BlocBuilder initiator. The experiments are denoted as *t*-BMA/AN-NHSBB-XX, where XX represents the initial molar feed concentration of AN given by f_{AN} : (a) *t*-BMA/AN-NHSBB-10, $f_{AN,0} = 0.094$; (b) *t*-BMA/AN-NHSBB-52, $f_{AN,0} = 0.52$ (refer to Table 16). The GPC was performed in THF at 40 °C using PS standards.

Figure 33: Number average molecular weight (M_n) versus conversion (X) for *tert*-butyl methacrylate/acrylonitrile (*t*-BMA/AN) copolymerizations performed in 50 wt% 1,4-dioxane solution at 90 °C with target molecular weights at complete conversion of 25 kg·mol⁻¹ using NHS-BlocBuilder at various AN feed concentrations, $f_{AN,0}$: $f_{AN,0} = 0.094$ (\diamondsuit), 0.30 (\blacktriangle), 0.52 (\blacksquare), 0.72 (\times) and 0.81 (\bigcirc).

Figure 34: Mayo plot showing acrylonitrile composition (F_{AN}) versus acrylonitrile initial molar feed composition ($f_{AN,0}$) for S/AN copolymers with NHS-BlocBuilder at 115 °C in 1,4-dioxane.

Figure 35: Mayo plot showing acrylonitrile composition (F_{AN}) versus acrylonitrile initial molar feed composition ($f_{AN,0}$) for *t*-BMA/AN copolymers with BlocBuilder/SG1 at 90 °C in 1,4-dioxane.

Figure 36: Kinetic plot of *t*-BMA/S/AN terpolymerizations with NHS-BlocBuilder at 90 °C in 50 wt% 1,4-dioxane with a molar feed composition of $f_{AN,0} = 0.50$, $f_{S,0} = 0.40$ and $f_{t-BMA,0} = 0.10$.

Figure 37: Gel permeation chromatograms of samples taken at various times for *t*-BMA/S/AN terpolymerization performed in 50 wt% 1,4-dioxane solution at 90 °C with $M_{n,target}$ at complete conversion of 25 kg·mol⁻¹ using NHS-BlocBuilder initiator. The

experiment is denoted as *t*-BMA/S/AN-NHSBB-10/50, which refers to *t*-BMA/S/AN terpolymerization done with NHS-BlocBuilder where 10 is the molar feed composition with respect to *t*-BMA and 50 is the molar feed composition with respect to AN. The GPC was performed in tetrahydrofuran (THF) at 40 °C using PS standards.

Figure 38: Number average molecular weight (M_n) versus conversion (X) for *t*-BMA/S/AN) terpolymerization performed with target molecular weights at complete conversion of 25 kg·mol⁻¹ using NHS-BlocBuilder at 90 °C with monomer feed concentration of: $f_{AN,0} = 0.50$, $f_{S,0} = 0.40$ and $f_{t-BMA,0} = 0.10$.

Figure 39: Procedure to produce amine-end functional styrene/acrylonitrile (S/AN) resins by first using NHS-BlocBuilder to initiate S/AN copolymerizations followed by a recovery step and then reaction with a diamine to yield the amine terminated polymer.

5.2 Manuscript Tables

Table 1: Experimental Conditions for Synthesis of Trioctylammonium p

 styrenesulfonate Homopolymers (poly(SS-TOA)) in Toluene

Experiment ID	T (°C)	$\phi_{Solution}{}^{\mathrm{a}}$	$M_{n,theoretical}$ (kg·mol ⁻¹)	[BB] ₀ (M)	[SG1] ₀ (M)	r^b	[SS-TOA] ₀ (M)	[Toluene] ₀ (M)
SS-TOA-90	90	0.20	20	0.011	0.001	0.085	0.40	9.44
SS-TOA-95	95	0.25	45	0.012	0.001	0.085	0.51	9.44
SS-TOA-100	100	0.21	20	0.012	0.001	0.084	0.44	9.44
SS-TOA-105	105	0.25	45	0.011	0.001	0.084	0.55	9.44

^a $\phi_{Solution}$ = weight fraction of SS-TOA monomer in SS-TOA/toluene solution mixture = mass SS-TOA/ (mass SS-TOA + mass toluene).

^b r = ratio of initial moles of SG1 to initial moles of BlocBuilder = [SG1]₀/ [BlocBuilder]₀.

Table 2: Experimental Conditions for Synthesis of Trioctylammonium pstyrenesulfonate/Styrene Random Copolymers (poly(SS-TOA-*ran*-S)) at 110 °C with Target Molecular Weight of 30 kg·mol⁻¹ in Toluene

Experiment ID	$\phi_{Solution}{}^{a}$	$f_{\rm SS-TOA,0}{}^{\rm b}$	[BB] ₀ (M)	[SG1] ₀ (M)	r ^b	[SS-TOA] ₀ (M)	[S] ₀ (M)	[Toluene] ₀ (M)
SS-TOA/S-10/90	0.45	0.11	0.015	0.001	0.084	0.33	3.01	6.19
SS-TOA/S-20/80	0.45	0.23	0.018	0.001	0.084	0.57	2.19	7.10
SS-TOA/S-30/70	0.35	0.32	0.013	0.001	0.084	0.51	1.24	8.10
SS-TOA/S-40/60	0.45	0.43	0.019	0.002	0.083	0.87	1.34	8.00
SS-TOA/S-50/50	0.35	0.50	0.014	0.001	0.084	0.67	0.78	8.60
SS-TOA/S-60/40	0.35	0.63	0.015	0.001	0.083	0.73	0.51	8.90
SS-TOA/S-80/20	0.35	0.80	0.015	0.001	0.083	0.85	0.24	9.18

^a $\phi_{Solution}$ = weight fraction of SS-TOA monomer in SS-TOA/toluene solution mixture = mass SS-TOA/ (mass SS-TOA + mass toluene).

 $^{b} f_{\text{SS-TOA}}$ is the initial molar feed composition of SS-TOA.

^c r = ratio of initial moles of SG1 to initial moles of BlocBuilder = [SG1]₀/ [BlocBuilder]₀.

Table 3: Kinetic Parameters for BlocBuilder/SG1 Nitroxide-Mediated Polymerization of Trioctylammonium p-styrenesulfonate and Styrene at Various Temperatures with Target Molecular Weight of 20 kg \cdot mol⁻¹ and 45 kg \cdot mol⁻¹ in Toluene^a

	Trioctylammonium	Trioctylammonium p-styrenesulfonate				
<i>T</i> (°C)	$\langle k_p \rangle [P] (10^5 \mathrm{s}^{-1})$	$\langle k_p \rangle [K] \ (10^6 \ {\rm s}^{-1})$	$\langle k_p \rangle [K] \ (10^6 \ {\rm s}^{-1})$			
90	2.0 ± 0.3	1.7 ± 0.3	0.9 ±- 0.1			
95	2.6 ± 0.5	2.2 ± 0.4	1.4 ± 0.2			
100	5.7 ± 0.9	4.8 ± 0.2	3.2 ± 0.2			
105	7.9 ± 0.9	6.7 ± 0.9	5.1 ± 0.3			

^a Kinetic parameters determined from initial slopes $\langle k_p \rangle [P \cdot]$ of semilogarithmic plots of $ln(1 - X)^{-1}$ versus time where X = conversion of monomer, $\langle k_p \rangle =$ propagation rate constant, and $[P \cdot] =$ concentration of growing chains. $\langle K \rangle$ is the equilibrium constant defined in *Equation 3*. Error bars are derived from the standard error of the slopes ($\langle k_p \rangle [P \cdot]$) from the linear fits of $ln(1 - X)^{-1}$ versus time.

Experiment ID	Conversion X	$M_{\rm n}({\rm kg}\cdot{ m mol}^{-1})$	$M_{ m w}/M_{ m n}$
SS-TOA-90	0.35	9.8	1.26
SS-TOA-95	0.28	15.9	1.20
SS-TOA-100	0.32	9.0	1.21
SS-TOA-105	0.34	15.2	1.18

Table 4: Summary of Conversions and Molecular Weight Characteristics for SS-TOA Homopolymers Synthesized at Various Temperatures with SG1/BlocBuilderInitiator in Toluene

Table 5: Summary of Compositions and Molecular Weight Characteristics forSS-TOA/StyreneCopolymersSynthesizedinTolueneat110°CwithSG1/BlocBuilderInitiator to Determine Reactivity Ratios of SS-TOA and Styrene

Experiment ID	$f_{_{ m SS-TOA,0}}{}^{ m a}$	$F_{ m SS-TOA}$ b	Conversion X	M_n (kg·mol ⁻¹)	$M_{ m w}/M_{ m n}$
SS-TOA/S-10/90	0.11	0.16	0.092	3.6	1.23
SS-TOA/S-20/80	0.23	0.30	0.101	2.9	1.21
SS-TOA/S-30/70	0.32	0.45	0.097	3.0	1.22
SS-TOA/S-40/60	0.43	0.73	0.098	3.0	1.26
SS-TOA/S-50/50	0.53	0.76	0.097	2.9	1.25
SS-TOA/S-60/40	0.63	0.85	0.095	2.9	1.25
SS-TOA/S-80/20	0.80	0.94	0.096	3.7	1.26

 ${}^{a}f_{\text{SS-TOA}}$ is the initial molar feed composition of SS-TOA.

^b F_{SS-TOA} is the final molar composition of SS-TOA determined using ¹H NMR.

Table 6: Summary of Monomer Reactivity Ratios by Three Methods forTrioctylamine Styrenesulfonate (SS-TOA)/Styrene Copolymerizations at 110 °Cwith SG1/BlocBuilder in Toluene

Method	r _{ss-toa}	r _{Styrene}	$r_{\rm SS-TOA}/r_{\rm Styrene}$
Fineman-Ross	4.43 ± 0.16	0.74 ± 0.03	5.99
Kelen-Tüdös	4.52 ± 0.68	0.77 ± 0.12	5.87
Regression	6.49 ± 0.06	1.10 ± 0.10	5.90

Table 7: Summary of Trioctylamine Styrene Sulfonate/Glycidyl MethacrylateGradient Copolymerization (SS-TOA/GMA) Conversions and Molecular WeightCharacteristics at 90 °C with NHS-BlocBuilder in Toluene

Sample	Time (min)	Conversion $X_{\rm SS-TOA}$	Conversion $X_{\rm GMA}$	Copolymer Composition F_{SS-TOA}	$M_{\rm n}$ (kg·mol ⁻¹)	$M_{ m w}/M_{ m n}$
Poly(SS-TOA) macroinitiator	220	0.25	0	-	2.1	1.28
Poly(SS-TOA- grad-GMA)	400	0.85	0.75	0.17	15.7	1.43

Experiment ID ^a	Feed composition $f_{_{ m AN,0}}$	[BB] ₀ (M)	[S] ₀ (M)	[AN] ₀ (M)	[Dioxane] ₀ (M)
S/AN-BB-10	0.10	0.019	4.38	0.48	5.46
S/AN-BB-30	0.30	0.019	3.77	1.61	5.41
S/AN-BB-40	0.40	0.019	3.46	2.29	5.30
S/AN-BB-50	0.50	0.019	3.01	3.10	5.29
S/AN-BB-70	0.70	0.018	2.07	4.72	5.30

Table 8: Styrene/Acrylonitrile (S/AN) Copolymerization Formulations forVarious Compositions using BlocBuilder at 90 °C in 1,4-Dioxane

^a All S/AN copolymerizations were done in 50 wt% 1,4-dioxane at 90 °C. S/AN-BB-xx refers to S/AN copolymerizations done with BlocBuilder where xx refers to molar feed composition with respect to AN.

Experiment ID ^a	Feed composition $f_{\rm AN,0}$	[NHSBB] ₀ (M)	[S] ₀ (M)	[AN] ₀ (M)	[Dioxane] ₀ (M)
S/AN-NHSBB-13	0.13	0.019	5.08	0.068	5.49
S/AN-NHSBB-20	0.20	0.019	4.81	0.11	5.49
S/AN-NHSBB-30	0.30	0.019	4.41	0.18	5.50
S/AN-NHSBB-39	0.39	0.019	4.01	0.24	5.51
S/AN-NHSBB-52	0.52	0.019	3.49	0.35	5.36
S/AN-NHSBB-70	0.70	0.019	2.41	0.53	5.31
S/AN-NHSBB-86	0.86	0.018	1.20	0.73	5.32

Table 9: Styrene/Acrylonitrile (S/AN) Copolymerization Formulations forVarious Compositions using NHS-BlocBuilder at 90 °C in 1,4-Dioxane

^a All S/AN copolymerizations were done in 50 wt% 1,4-dioxane a 90 °C. S/AN-NHSBB-xx refers to S/AN copolymerizations done with NHS-BlocBuilder where xx refers to molar feed composition with respect to AN.

Table 10: Tert-Butyl-methacrylate/Acrylonitrile (t-BMA/AN) CopolymerizationFormulations for Various Compositions using BlocBuilder/SG1 at 90 °C in 1,4-Dioxane

Experiment ID ^a	Feed composition $f_{AN,0}$	[BB] ₀ (M)	[SG1] ₀ (M)	r^b	[<i>t</i> -BMA] ₀ (M)	[AN] ₀ (M)	[Dioxane] ₀ (M)
t-BMA/AN-BB/SG1-11	0.11	0.021	0.002	0.081	3.54	0.44	4.92
t-BMA/AN-BB/SG1-30	0.30	0.019	0.002	0.080	2.86	1.21	5.30
t-BMA/AN-BB/SG1-51	0.51	0.019	0.002	0.085	2.47	2.57	4.98
t-BMA/AN-BB/SG1-70	0.70	0.019	0.002	0.081	1.80	4.17	5.06
t-BMA/AN-BB/SG1-80	0.80	0.019	0.002	0.080	1.34	5.46	5.01

^a All *t*-BMA/AN copolymerizations were done in 50 wt% 1,4-dioxane at 90 °C. *t*-BMA/AN-NHSBB-xx refers to *t*-BMA/AN copolymerizations done with BlocBuilder/SG1 where xx refers to molar feed composition with respect to AN. ^b r = ratio of initial moles of SG1 to initial moles of BlocBuilder = [SG1]₀/

[BlocBuilder]₀.

Table 11: Tert-Butyl-methacrylate/Acrylonitrile (t-BMA/AN) CopolymerizationFormulations for Various Compositions using NHS-BlocBuilder at 90 °C in 1,4-Dioxane

Experiment ID ^a	Feed composition $f_{AN,0}$	[NHSBB] ₀ (M)	[<i>t</i> -BMA] ₀ (M)	[AN] ₀ (M)	[Dioxane] ₀ (M)
t-BMA/AN-NHSBB-10	0.10	0.019	3.21	0.33	5.35
t-BMA/AN-NHSBB-30	0.30	0.019	2.84	1.24	5.36
t-BMA/AN-NHSBB-52	0.52	0.019	2.28	2.54	5.43
t-BMA/AN-NHSBB-72	0.72	0.018	1.64	4.35	5.27
t-BMA/AN-NHSBB-81	0.81	0.019	1.25	5.37	5.23

^a All *t*-BMA/AN copolymerizations were done in 50 wt% 1,4-dioxane at 90 °C. *t*-BMA/AN-NHSBB-xx refers to *t*-BMA/AN copolymerizations done with NHS-BlocBuilder where xx refers to molar feed composition with respect to AN.

Table 12: *Tert*-Butyl-methacrylate/Styrene/Acrylonitrile (*t*-BMA/S/AN)Terpolymerization Formulation at 90 °C in 1,4-Dioxane

Experiment ID ^a	[NHSBB] ₀	[<i>t</i> -BMA] ₀	[S] ₀	[AN] ₀	[Dioxane] ₀
	(M)	(M)	(M)	(M)	(M)
t-BMA/S/AN/-NHSBB-10/50	0.019	0.58	4.16	2.92	5.32

^a The *t*-BMA/S/AN terpolymerization was done in 50 wt% 1,4-dioxane at 90 °C. *t*-BMA/S/AN-NHSBB-xx/yy refers to *t*-BMA/S/AN done with NHS-BlocBuilder where xx refers to molar feed composition with respect to *t*-BMA and yy refers to molar feed composition of AN.

Experiment ID ^a	Feed composition $f_{AN,0}$	Copolymer composition ^b F_{AN}	Conversion X	$M_{\rm n}$ (kg·mol ⁻¹) ^c	$M_{ m w}/M_{ m n}^{\ c}$
S/AN-BB-10	0.10	0.22	0.42	13.6	1.23
S/AN-BB-30	0.30	0.38	0.43	16.0	1.17
S/AN-BB-40	0.40	0.44	0.40	15.3	1.18
S/AN-BB-50	0.50	0.46	0.28	13.2	1.18
S/AN-BB-70	0.70	0.52	0.32	10.7	1.26

 Table 13: Summary of Compositions and Molecular Weight Characteristics of

 Poly(styrene-*ran*-acrylonitrile) Copolymers Initiated from BlocBuilder

^a All S/AN copolymerizations were done in 50 wt% 1,4-dioxane at 90 °C. S/AN-BB-xx refers to S/AN copolymerizations done with BlocBuilder where xx refers to molar feed composition with respect to AN.

^b Copolymer composition determined using Fourier transform infrared (FTIR) spectroscopy.

^c Weight average molecular weight (M_w), number average molecular weight (M_n) and polydispersity index (M_w/M_n) determined using gel permeation chromatography (GPC) relative to linear PMMA standards in dimethylformamide (DMF) at 50 °C after correction using composition averaged Mark-Houwink parameters of poly(acrylonitrile) and poly(styrene) in DMF.

Experiment ID ^a	Feed composition $f_{\rm AN,0}$	Copolymer composition ^b F_{AN}	Conversion X	$M_{ m n}$ $(m kg\cdot m mol^{-1})^{ m c}$	$M_{ m w}/M_{ m n}^{ m c}$
S/AN-NHSBB-13	0.13	0.17	0.59	11.7	1.26
S/AN-NHSBB-20	0.20	0.26	0.52	11.9	1.19
S/AN-NHSBB-30	0.30	0.34	0.63	13.6	1.25
S/AN-NHSBB-39	0.39	0.42	0.72	16.4	1.14
S/AN-NHSBB-52	0.52	0.46	0.76	18.1	1.18
S/AN-NHSBB-70	0.70	0.50	0.55	14.7	1.25
S/AN-NHSBB-86	0.86	0.52	0.47	10.6	1.26

Table 14: Summary of Compositions and Molecular Weight Characteristics ofPoly(styrene-*ran*-acrylonitrile) Copolymers Initiated by NHS-BlocBuilder

^a All S/AN copolymerizations were done in 50 wt% 1,4-dioxane a 90 °C. S/AN-NHSBB-xx refers to S/AN copolymerizations done with N-hydroxysuccinimide terminated BlocBuilder where xx refers to molar feed composition with respect to AN.

^b Copolymer composition determined using Fourier transform infrared (FTIR) spectroscopy.

^c Weight average molecular weight (M_w), number average molecular weight (M_n) and polydispersity index (M_w/M_n) determined using gel permeation chromatography (GPC) relative to linear PMMA standards in dimethylformamide (DMF) at 50 °C after correction using composition averaged Mark-Houwink parameters of poly(acrylonitrile) and poly(styrene) in DMF.

Table 15: Summary of Compositions and Molecular Weight Characteristics ofPoly(tert-butyl methacrylate-ran-acrylonitrile)CopolymersInitiated fromBlocBuilder with an excess of SG1 (r = 8.0-8.5 mol%)

Experiment ID ^a	Feed composition $f_{AN,0}$	Copolymer composition ^b F_{AN}	Conversion X	$M_{ m n}$ $(m kg\cdot mol^{-1})^{ m c}$	$M_{ m w}/M_{ m n}^{ m c}$
t-BMA/AN-BB/SG1-11	0.11	0.12	0.66	14.8	1.40
t-BMA/AN-BB/SG1-30	0.30	0.22	0.57	11.9	1.35
t-BMA/AN-BB/SG1-51	0.51	0.27	0.51	11.4	1.33
t-BMA/AN-BB/SG1-70	0.70	0.34	0.32	5.0	1.24
t-BMA/AN-BB/SG1-80	0.80	0.37	0.20	4.7	1.17

^a All *t*-BMA/AN copolymerizations were done in 50 wt% 1,4-dioxane at 90 °C. *t*-BMA/AN-NHSBB-xx refers to *t*-BMA/AN copolymerizations done with BlocBuilder/SG1 where xx refers to molar feed composition with respect to AN. ^b Copolymer composition determined using Fourier transform infrared (FTIR)

spectroscopy.

^c Weight average molecular weight (M_w) , number average molecular weight (M_n) and polydispersity index (M_w/M_n) determined using gel permeation chromatography (GPC) relative to linear PS standards in tetrahydrofuran (THF) at 40 °C.

Table 16: Summary of Compositions and Molecular Weight Characteristics of

 Poly(*tert*-butyl methacrylate-*ran*-acrylonitrile)

 Copolymers Initiated from NHS

 BlocBuilder

Experiment ID ^a	Feed composition $f_{AN,0}$	Copolymer composition ^b F_{AN}	Conversion X	$M_{ m n}$ $(m kg\cdot m mol^{-1})^{ m c}$	$M_{ m w}/M_{ m n}^{ m c}$
t-BMA/AN-NHSBB-10	0.094	0.096	0.73	14.8	1.40
t-BMA/AN-NHSBB-30	0.30	0.22	0.80	15.6	1.42
t-BMA/AN-NHSBB-52	0.52	0.26	0.61	15.4	1.30
t-BMA/AN-NHSBB-72	0.72	0.33	0.32	11.1	1.50
t-BMA/AN-NHSBB-81	0.81	0.35	0.21	7.7	1.23

^a All *t*-BMA/AN copolymerizations were done in 50 wt% 1,4-dioxane at 90 °C. *t*-BMA/AN-NHSBB-xx refers to *t*-BMA/AN copolymerizations done with NHS-BlocBuilder where xx refers to molar feed composition with respect to AN.

^b Copolymer composition determined using Fourier transform infrared (FTIR) spectroscopy.

^c Weight average molecular weight (M_w) , number average molecular weight (M_n) and polydispersity index (M_w/M_n) determined using gel permeation chromatography (GPC) relative to linear PS standards in tetrahydrofuran (THF) at 40 °C.

Experiment ID ^a	Feed composition $f_{AN,0}$ $f_{t-BMA,0}$	Copolymer composition ^b F_{AN} F_{t-BMA}	Conversion X	$M_{ m n}$ $(m kg\cdot mol^{-1})^{ m c}$	$M_{ m w}/M_{ m n}^{ m c}$
<i>t</i> -BMA/S/AN- NHSBB-10/50	0.50 0.10	0.47 0.11	0.54	13.6	1.19

 Table 17: Summary of Compositions and Molecular Weight Characteristics of

 Poly(t-BMA-ran-S-ran-AN) Terpolymer Initiated from NHS-BlocBuilder

^a The *t*-BMA/S/AN terpolymerization was done in 50 wt% 1,4-dioxane at 90 °C. *t*-BMA/S/AN-NHSBB-xx/yy refers to *t*-BMA/S/AN terpolymerizations done with NHS-BlocBuilder where xx refers to molar feed composition with respect to *t*-BMA and yy refers to molar feed composition with respect to AN.

^b Copolymer composition determined using Fourier transform infrared (FTIR) spectroscopy.

^c Weight average molecular weight (M_w) , number average molecular weight (M_n) and polydispersity index (M_w/M_n) determined using gel permeation chromatography (GPC) relative to linear PS standards in tetrahydrofuran (THF) at 40 °C.

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