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Versatility of a Succinimidyl-Ester Functional Alkoxyamine for Controlling Acrylonitrile Copolymerizations

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ABSTRACT

Styrene/acrylonitrile (S/AN) and *tert*-butyl methacrylate/acrylonitrile (*t*BMA/AN) copolymers were synthesized in a controlled manner (low polydispersity $\overline{M}_w/\overline{M}_n$ with linear growth of number average molecular weight $\overline{M}_n$ versus conversion X) by nitroxide mediated polymerization (NMP) with a succinimidyl ester (NHS) terminated form of BlocBuilder unimolecular initiator (NHS-BlocBuilder) in dioxane solution. No additional free nitroxide (SG1) was required to control the *t*BMA-rich copolymerizations with NHS-BlocBuilder, a feature previously required for methacrylate polymerizations with BlocBuilder initiators. Copolymers from S/AN mixtures (AN molar initial fractions $f_{AN,0}$= 0.13-0.86, T = 115 ºC) had $\overline{M}_w/\overline{M}_n$ = 1.14-1.26 and linear $\overline{M}_n$ versus conversion X up to $X \approx 0.6$. *t*BMA/AN copolymers ($f_{AN,0}$= 0.10-0.81, T = 90 ºC) possessed slightly broader molecular weight distributions ($\overline{M}_w/\overline{M}_n$ = 1.23-1.50), particularly as the initial composition became richer in *t*BMA, but still exhibited linear plots of $\overline{M}_n$ versus conversion X up to $X \approx 0.6$. A S/AN/*t*BMA terpolymerization ($f_{AN,0}$= 0.50, $f_{S,0}$ = 0.40) was also conducted at 90 ºC and revealed excellent control with $\overline{M}_n$= 13.6 kg·mol^{-1}, $\overline{M}_w/\overline{M}_n$= 1.19, and linear $\overline{M}_n$ versus conversion X up to X = 0.54. Incorporation of AN and *t*BMA in the final copolymer (molar composition F_{AN} = 0.47, $F_{t\mathrm{BMA}}$ = 0.11) was similar to the initial composition and represents initial designs to make tailored, acid functional AN copolymers by NMP for barrier materials.

Keywords: copolymerization; radical polymerization; polymerization kinetics, nitroxide mediated polymerization; acrylonitrile.

INTRODUCTION

Controlled radical polymerization (CRP) has dramatically aided, and in several cases, has made only possible, the synthesis of various copolymers of controlled architecture of interest for many modern technologies. For example, certain monomers can only be combined by CRP and cannot be accessed by more traditional methods to make copolymers of controlled architecture, such as ionic polymerization.[1] Furthermore, CRP can be easily accommodated in many existing conventional free radical polymerization processes.[2] Consequently, it is becoming increasingly the method of choice to make polymeric materials with controlled microstructure.

Acrylonitrile is a widely used monomer applied towards the manufacture of resins for carbon fibers[3-5] and separation membranes/barrier materials.[6-9] For example, styrene/acrylonitrile (S/AN) copolymers made by conventional radical copolymerization have long been used as barrier materials where styrene offers good processing behavior and AN provides excellent grease resistance.[10] AN-containing copolymers may be suitable barrier materials for poly(ethylene) (PE) matrices. Previously, materials such as nylon have been used as barrier polymers in such blends where the nylon is dispersed as elongated domains in the PE matrix. The morphology of such nylon/PE blends was stabilized by formation of copolymer via reaction between the amino groups inherent on the nylon chain ends and anhydride groups that were grafted onto PE.[11-13] However, alternative AN-containing copolymers as barriers for PE have not been examined widely despite the possibility of polymerizing AN using CRP. Further, such AN-containing copolymers must have suitable functional groups to be used in reactive blends with PE and such functional groups can be accessed via the initiator residues from the CRP process.

Several examples of AN copolymers made by CRP with sophisticated architectures and control of molecular weight are noted in the literature. For example, atom transfer radical polymerization (ATRP) has been used to make S/AN copolymers as a precursor to porous carbon monoliths (the AN can be cross-linked at higher temperatures to form ladder-type matrices).[4] Activator regenerated by electron transfer (ARGET) ATRP of AN has also allowed access to poly(acrylonitrile) resins.[14,15] Nitroxide mediated polymerization (NMP) has also been effective at controlling AN polymerizations.[16-23] Further, like S and other styrenic-based monomers, AN serves as an effective controlling co-monomer for methacrylate-rich copolymerizations using alkoxyamines such as SG1 and BlocBuilder (Scheme 1). This traditionally was not possible for NMP using first-generation nitroxides such as TEMPO.[24] In addition to acting as a controller for methacrylate-rich polymerizations by NMP, AN imparts desirable properties to the copolymer such as enhanced water-solubility.[25]

Altering the initiator structure can permit access to alternative copolymers and reactive groups. For example, reacting BlocBuilder with *N*-hydroxysuccinimide (NHS) yielded the succinimidyl ester terminated BlocBuilder (see Scheme 1c) that can be reacted appropriately further with diamines to give amino functional end groups, for example.[26] Thus, we studied initially here S/AN copolymerizations using the succinimidyl ester form of BlocBuilder (NHS-BlocBuilder), to form copolymers which could be further reacted with a diamine to provide S/AN copolymers with varying AN content and the desirable group for reactive blending. Second, we used AN as a controlling co-monomer for *t*BMA/AN copolymerizations with NHS-BlocBuilder (*t*BMA was used as the precursor to methacrylic acid, which can subsequently be used as functional group for reactive blending). Our previous study using NHS-BlocBuilder required no additional SG1 free nitroxide to provide sufficient control of the polymerization[27,28], as has been the case for methacrylate copolymerizations with BlocBuilder.[29-34] Thus, in addition to gaining the utility of the NHS-group, the use of NHS-BlocBuilder could also greatly simplify future methacrylate-rich formulations sought by NMP methods. We finally concluded our studies by examining S/AN/*t*BMA terpolymerizations mediated by NHS-BlocBuilder as a potential precursor for S/AN copolymers with methacrylic acid functionality located at random positions along the chain. The resulting terpolymer could then be used as a starting point for future designs of tailored AN-containing resins desirable for barrier applications.

EXPERIMENTAL

Materials

Acrylonitrile (AN, 99%), styrene (S, 99%) and *tert*-butyl methacrylate (*t*BMA, 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 used as received. *N*-

hydroxysuccinimide (98%) and *N,N'*-dicyclohexylcarbodiimide (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.[26] Poly(styrene) (PS, number average molecular weight $\bar{M}_n$ = 13.0 kg·mol^{-1}, polydispersity index $\bar{M}_w/\bar{M}_n$ = 1.10), poly(acrylonitrile) (PAN, $\bar{M}_n$ = 60.6 kg·mol^{-1}, $\bar{M}_w/\bar{M}_n$= 1.70), and poly(*t*-butyl methacrylate) (P*t*BMA, $\bar{M}_n$ = 38.5 kg·mol^{-1}, $\bar{M}_w/\bar{M}_n$= 1.01) were used as standards for Fourier transform infrared spectroscopy (FTIR) and were obtained from Scientific Polymer Products Inc.

Synthesis of Styrene/Acrylonitrile Random Copolymers with NHS-BlocBuilder

Several nitroxide mediated copolymerization experiments of styrene (S) and acrylonitrile (AN) in 1,4-dioxane were conducted at 115°C using 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 initial compositions, $f_{\mathrm{AN},0}$, from 0.13-0.86 were followed and are found in Table 1. All polymerizations were conducted in 50 wt% 1,4-dioxane solutions (50 wt% of monomer in solvent). The target number average molecular weight ($\bar{M}_{n,\,target}$) at complete conversion, calculated by the mass of monomer relative to the moles of 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-NHSBB-30, NHS-BlocBuilder (0.099 g, 0.21 mmol) and the stirrer were added to the flask, which was then sealed with a rubber septum. Previously purified styrene (4.29 g, 41.3 mmol), acrylonitrile (0.933 g, 17.6 mmol) and 1,4-dioxane (5.34 g, 60.7 mmol) were each injected into the flask via syringe. 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 115°C at a rate of about $5°\mathrm{C}\cdot\mathrm{min}^{-1}$ 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 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-NHSBB-30, the final yield after 400 minutes was 3.0 g (63% conversion based on gravimetry) with number-average molecular weight $\bar{M}_n = 13.6\ \mathrm{kg}\cdot\mathrm{mol}^{-1}$ and polydispersity index $\bar{M}_w/\bar{M}_n = 1.25$ determined by gel permeation chromatography calibrated relative to linear PMMA standards in DMF at 50°C and corrected with compositionally averaged Mark-Houwink parameters for the SAN copolymers (see *Characterization* section for further details). The AN molar composition of the S/AN copolymer for the particular sample using FTIR was $F_{AN} = 0.34$.

Synthesis of tert-Butyl Methacrylate/Acrylonitrile Random Copolymers (poly(tBMA-ran-AN))

Nitroxide mediated copolymerizations of *t*BMA with AN in 1,4-dioxane were conducted at 90°C using 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 as indicated in the previous section. Formulations for initial molar initial compositions, $f_{AN,0}$, from 0.10-0.81, can be found in Table 2. All polymerizations were conducted in 50 wt% 1,4-dioxane solutions. Target molecular weights at complete conversion ($\bar{M}_{n,\,target}$), calculated based on the mass of *t*BMA and AN monomers relative to NHS-BlocBuilder initiator, were nearly 25 kg·mol^{-1} for all experiments. Initiator, solvent and monomer were added to the flask with the stirrer. As an example, for experiment ID *t*BMA/AN-BB-30, NHS-BlocBuilder (0.0993 g, 0.208 mmol) was added to the flask, which was then sealed with a rubber septum. *t*BMA (4.47 g, 31.4 mmol), acrylonitrile (0.727 g, 13.7 mmol) and 1,4-dioxane (5.214 g, 59.3 mmol) were each injected into the flask using disposable 5 mL syringes. After purging with nitrogen for 30 min at room temperature, the reactor was then heated to 90°C at a rate of about 5°C·min^{-1} while maintaining the purge. During the polymerization, samples were collected at periodic intervals, cooled and 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-NHSBB-30, the final yield after 250 minutes was 3.30 g (64% conversion based on gravimetry) with number-average molecular weight $\bar{M}_n$= 15.6 kg·mol^{-1} with polydispersity index of $\bar{M}_w/\bar{M}_n$= 1.42 determined by gel permeation chromatography calibrated with linear poly(styrene) standards in THF at 40°C and corrected with compositionally averaged Mark-Houwink parameters. The composition of the particular *t*BMA/AN copolymer for experiment ID *t*BMA/AN-NHSBB-30 was F_{AN} = 0.22.

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

A nitroxide mediated terpolymerization of *t*BMA, S and AN in 50 wt% 1,4-dioxane solution was conducted at 90°C. A similar experimental procedure used for the S/AN and *t*BMA/AN copolymerizations was applied for the *t*BMA/S/AN terpolymerization. *t*BMA (1.83 g, 12.9 mmol), styrene (5.20 g, 50.0 mmol) and AN (3.40 g, 64.1 mmol) were each injected in the flask with NHS-BlocBuilder (0.197 g, 0.41 mmol) in a 50 wt% solution of 1,4-dioxane (10.3 g, 117 mmol). Over the course of the reaction, samples were taken periodically with a 1 mL syringe and precipitated in hexane to recover the polymer. 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 $\bar{M}_n$ = 13.5 kg·mol^{-1} and $\bar{M}_w/\bar{M}_n$= 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. The terpolymer molar composition was F_{AN} = 0.47 and F_{tBMA} = 0.11 according to FTIR using the set of PS, PAN and P*t*BMA standards as markers for the functional groups in the terpolymer.

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 at relatively high AN loadings (≈ 52 mol% AN) and tetrahydrofuran (THF) was used as the mobile phase for *t*BMA/AN copolymers (the copolymers were soluble in THF at the compositions studied - the AN concentrations in the copolymers were all below ≈ 35 mol%). The applied flow rate was 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 against 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 $[\eta] = KM^{\alpha}$, based on the following coefficients. For the *t*BMA/AN copolymers in THF, we took the solution properties of the copolymer to be essentially that of poly(*t*BMA) in THF (since the AN incorporation in the copolymer was relatively low). Thus, using $K_{PS} = 11.4 \times 10^{-5}$ dL·g^{-1} and $\alpha_{PS} = 0.716$ in THF at 40°C[35] and $K_{PtBMA} = 11.2 \times 10^{-5}$ dL·g^{-1} and $\alpha_{PtBMA} = 0.692$ in THF at 30°C[36], we performed universal calibration against PS standards in THF (note that poly(acrylonitrile) (PAN) was not soluble in THF, so compositionally averaging Mark-Houwink coefficients from the homopolymers was not possible). Obviously, there is error associated using such estimates. For S/AN copolymers in DMF at various AN compositions (F_{AN}), Mark-Houwink parameter to estimate S/AN copolymer molecular weights were available: $K_{\mathrm{SAN}} = 1.62 \times 10^{-4}$ dL·g^{-1} and $\alpha_{\mathrm{SAN}} = 0.75$ ($F_{AN} = 0.40$, T = 30 °C)[37] and $K_{\mathrm{SAN}} = 1.2 \times 10^{-4}$ dL·g^{-1} and $\alpha_{\mathrm{SAN}} = 0.77$ ($F_{AN} = 0.626$, T = 30 °C).[38] Mark-Houwink parameters for SAN copolymers were not however available at higher temperatures used to ensure solubility. Therefore, since Mark-Houwink coefficients from PS and PAN homopolymers are available at various temperatures, the homopolymer Mark-Houwink coefficients at 50 °C can be estimated ($K_{\mathrm{PS,50^oC}} = 2.82 \times 10^{-4}$ dL·g^{-1}, $\alpha_{\mathrm{PS,50^oC}} = 0.615$ from data provided by Tsimpris et al. up to 45 °C[39] and from Dalal at 60 °C[40]; $K_{\mathrm{PAN,50^oC}} = 3.0 \times 10^{-4}$ dL·g^{-1}, $\alpha_{\mathrm{PAN,50^oC}} = 0.752$ from data first provided by Fujisaki et al at 50°C[41]) and then used to obtain compositionally-averaged Mark-Houwink coefficients representing the solution properties of the SAN copolymers. For the PMMA standards, $K_{\mathrm{PMMA}} = 2.07 \times 10^{-5}$ dL·g^{-1} and $\alpha_{\mathrm{PMMA}} = 0.632$ in DMF at 50°C.[42] Fourier transform infrared spectroscopy (FTIR) (Spectrum BX, Perkin-Elmer) was used to determine the molar compositions 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 PS, PAN and P*t*BMA standards.

RESULTS AND DISCUSSION

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 and no additional free nitroxide was required in the latter case.[26] It has been further examined to be suitable in controlling methacrylate-rich compositions without the need of additional free nitroxide, a feature that was thought to be generally required for NMP of methacrylates. Before examining its suitability for controlling methacrylic polymerizations, we first sought to examine the suitability of NHS-BlocBuilder for controlling S/AN copolymerizations, beginning with experiments at 115 °C in 50 wt% 1,4-dioxane solutions, without any added free nitroxide. Although S/AN copolymerizations were previously found to be controlled sufficiently by BlocBuilder alone[27] the possibility of using the succinimide end group for further modification is highly desirable. For example, reaction of diamines with the NHS-terminated SAN to make primary amine-functionalized SAN is highly desirable for reactive blending/modification. Figure 1 shows the semi-logarithmic plots of $ln(1-X)^{-1}$ versus time of S/AN copolymerizations with $f_{AN,0}$ = 0.13-0.86. Such plots are useful for determining the apparent rate constant $\langle \boldsymbol{k_p} \rangle$ [P·], where $\langle \boldsymbol{k_p} \rangle$is the average propagation rate constant and [P·] is the concentration of propagating macroradicals. This plot is derived below by writing the expression for the rate of polymerization (i.e. the rate of monomer consumption) as a function of the concentration of monomer [M] at any time and the initial monomer concentration $[M]_0$.

$$\frac{d[M]}{dt} = -\langle k_p \rangle [P\cdot][M] \qquad [1]$$

$$[M] = [M]_0 (1-X) \qquad [2]$$

Inserting [2] into [1] thus provides the following expression, which was used to derive the apparent rate constants.

$$\begin{aligned} \frac{d(1-X)}{dt} &= -\frac{dX}{dt} = -\langle k_p \rangle [P\cdot](1-X) \\ -\frac{dX}{(1-X)} &= -\langle k_p \rangle [P\cdot] dt \end{aligned} \qquad [3]$$

After integrating, the expression becomes the following.

$$\ln\left[\frac{1}{1-X}\right] = \langle k_p \rangle [P\cdot] t \qquad [4]$$

All plots were linear and extraction of the apparent rate constants from the plots indicate that increasing AN initial content resulted in $\langle k_p \rangle$[P·] = (6.9 ± 0.4) × 10^{-5} s^{-1} at $f_{AN,0}$ = 0.13 to $\langle k_p \rangle$[P·] = (2.8 ± 0.5) × 10^{-5} s^{-1} at $f_{AN,0}$ = 0.86, which is in the range for that reported for S/AN copolymerizations using BlocBuilder earlier (except that the temperature here was higher).[27] There was not expected to be much variation in the kinetics on increasing AN initial content and that was the case here. At 115 °C, the homopropagation k_p for AN is estimated from Junker et al's pulsed laser polymerization (PLP) experiments to be 1.5 x 10^4 L·mol^{-1}·s^{-1} [43] while the k_p for S is estimated from PLP measurements to be 1.8 x 10^3 L·mol^{-1}·s^{-1} [44] at 115 °C. The other factor modulating the polymerization rate is the equilibrium constant K between dormant and active chains. For S NMP with SG1-type initiators, $K_S \approx 2.2 \times 10^{-9}$ mol·L^{-1} [45] while that for AN was suggested to be similar to that of n-butyl acrylate by Nicolas et al and is estimated to be $K_{AN} \approx 1 \times 10^{-10}$ mol·L^{-1} at 115 °C.[21] The combination of k_pK is readily related to $\langle k_p \rangle[P^\cdot]$ given some assumptions and is often used as a measure for the control of the nitroxide mediated polymerization.[21,46] Given the data available for k_p and K, $(k_pK)_S$ (115 °C) ≈ 4 x10^{-6} s^{-1} and $(k_pK)_{AN}$ (115 °C) ≈ 2 x10^{-6} s^{-1}, there should not be a large variation in the kpK as a function of composition. This was corroborated by the data which indicates $\langle k_p \rangle[P^\cdot]$ for the NHS-BlocBuilder mediated S/AN copolymerizations did not change much over most of the compositions up to about $f_{AN,0} \approx 0.6$ (Figure 2).

There are some deviations for the S/AN copolymerizations observed in the kinetic plots shown in Figure 1. Obviously, using gravimetry to measure conversion must be carefully applied. This may also result in some fractionation of the samples taken at low conversion (early polymerization times). Further, assuming that the initial time was set to when the reactor temperature reached 115 °C, it is possible that polymerization was already occurring at temperatures below 115 °C. Thus, there is some considerable error at early stages possible. Also, at high AN feed compositions (i.e. $f_{AN,0}$ = 0.70 and 0.86) it is possible that the polymerization becomes heterogeneous and the AN-rich copolymer begins to precipitate out the solution. This has been reported elsewhere for AN polymerizations[47-50]. Finally, it should be noted that it is possible that other effects such as inhibition and autoinitiation could be occurring. Autoinitiation was reported for S/AN copolymerizations by Hasha et al[51] while autoacceleration was observed for S/AN copolymerizations by Sebastian and Biesenberger[52]. In the latter case, the effect is more pronounced at higher AN feed compositions. Induction periods have been suggested for controlled radical S/AN copolymerizations based on examinations of S/maleic anhydride copolymerizations with TEMPO[53]. A Diels-Alder reaction followed by hydrogen abstraction to either monomer or TEMPO was cited as the initiation reaction to overcome the induction period due to TEMPO. We do not expect as dramatic effects as for TEMPO since BlocBuilder type initiators are much more labile. Thus, the kinetics may be more complicated and coupled with the experimental difficulties with S/AN copolymerizations here, the apparent rate constants may obscure some phenomena and could be subject to considerable error.

GPC analysis of samples taken during the polymerization indicated that in all cases, the S/AN copolymers possessed narrow molecular weight distributions with low M_w/M_n ranging from 1.14-1.26 (Figure 3) and were characterized by steady, monomodal shifts in the distribution. The S/AN copolymerizations also exhibited relatively linear M_n versus X plots (Figure 4). The plots were linear up to about 60% conversion ($M_n \approx 18$ $kg{\cdot}mol^{-1}$), indicating a controlled polymerization was approached. The molecular weight characteristics and final copolymer compositions are summarized in Table 3.

***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[26] and consequently we predict that the NHS-group can serve not only as a functional group to further derivatize the chains but that the NHS-BlocBuilder can sufficiently release enough SG1 from the start of the reaction to effectively control *t*-BMA-rich copolymerizations as we indicated for glycidyl methacrylate-rich copolymerizations[34]. Additionally, it is highly advantageous from a scale-up perspective to simplify the formulation and avoid the use of additional free nitroxide, as we had to earlier with *t*BMA/AN copolymerizations with BlocBuilder.[27] *t*BMA/AN copolymerizations ($f_{\mathrm{AN},0}$ = 0.094-0.81) synthesized in 50 wt% 1,4-dioxane solutions at 90°C with M_n at complete conversion of 25 kg·mol^{-1}, show that NHS-BlocBuilder could effectively control the polymerizations for *t*BMA-rich compositions. Note that a lower temperature for tBMA/AN copolymerizations was used compared to S/AN copolymerizations since the methacrylate-rich compositions require lower temperatures to be effectively controlled.[29-31] In Figure 5, the semi-logarithmic plots of $ln(1-X)^{-1}$ versus time for *t*-BMA/AN copolymerizations with $f_{\mathrm{AN},0}$ ranging from 0.10-0.81 show that conversion increased with a relatively linear trend up to ≈ 60%. Extraction of the apparent rate constants, $\langle \boldsymbol{k_p} \rangle$[P·], from the slopes of the plots in the linear regions in Figure 5 indicated that increasing AN initial concentration tended to decrease the apparent rate constant from $(6.8 \pm 0.4) \times 10^{-5}$ s^{-1} at $f_{AN,0}$ = 0.094 to $(5.4 \pm 0.5) \times 10^{-6}$ s^{-1} at $f_{AN,0}$ = 0.81 (see plots in Figure 6). These values are slightly higher than those estimated for *t*BMA/AN copolymerizations using BlocBuilder/SG1[27] but they are again reasonable as the estimated range of k_p[P·] values mirror the difference in k_p*s* of AN and *t*BMA available in the literature as reported by Junkers et al.[43] and Roberts et al.[54] respectively and the K_{AN}[21] and K_{tBMA}[55] estimated from the literature. From these sources, the combined parameter k_pK for AN at 90 °C is estimated to be 1.1×10^{-7} s^{-1} while k_pK for *t*BMA at 90 °C was estimated to be 4.2×10^{-4} s^{-1}. For MMA polymerizations controlled by AN with $f_{AN,0} = 0.088$ using BlocBuilder/SG1 at 90 °C, $k_pK = 2.6 \times 10^{-6}$ s^{-1}, which indicates the dramatic effect of adding only a small amount of AN to control a methacrylate-rich NMP process.[21] The results for the *t*BMA/AN copolymerization are in sharper contrast compared to the S/AN copolymerizations with NHS-BlocBuilder discussed previously and can be ascribed to the very high K of the methacrylate[56] relative to that of S or AN.

Extraction of kinetic data from the plots of Figure 5 for *t*BMA/AN copolymerizations could also be subject to some of the same issues for the S/AN copolymerization studied earlier. We note the experimental limitations (use of gravimetry, dissociation of initiator begin before set point temperature reached) and the possibility of autoinitiation/autoacceleration effects for the copolymerization. However, it should be noted that forcing the data through the origin might suggest that inhibition/autoinitiation are the sole reasons for the observed trends. For example, the data at $f_{AN,0} = 0.094$ and $f_{AN,0} = 0.30$ suggest that some sort of exponential growth and plateau is occurring. In these cases, the faster polymerization rates due to the relatively rich *t*BMA feed suggest that the polymerization could have been occurring already before the temperature set point was attained. This fast polymerization might also be aided by the faster decomposition of the NHS-BlocBuilder initiator. In contrast, at richer AN feed compositions, such as at $f_{AN,0} = 0.52$ and $f_{AN,0} = 0.72$, may seem to indicate some sort of inhibition. However, the polymerization rates are very slow at these AN-rich compositions, as expected and it is difficult to discern a clear inhibitory effect. Also, the AN-rich copolymers at early polymerizations may be essentially oligomers and when precipitated, can be easily washed out, and suggest a lower conversion than what it should be.

The molecular weights for the *t*BMA/AN copolymers controlled with NHS-BlocBuilder were determined by GPC relative to linear poly(styrene) standards in THF at 40°C. Thus the results were converted to the corresponding copolymer M_n based on using Mark-Houwink parameters for poly(*t*BMA) since the copolymers were soluble in THF and did not incorporate much AN (See *Characterization* section and only up to ≈ 35 mol% AN was incorporated in the final copolymers for a initial composition of 80 mol% AN (Experiment ID: *t*BMA/AN-NHSBB-81 in Table 4)). GPC analysis of samples taken during the polymerization indicated in most cases that *t*BMA/AN copolymers possessed narrow molecular weight distributions with $\bar{M}_w/\bar{M}_n$ranging from 1.23-1.50 (Figure 7) and exhibited relatively linear $\bar{M}_n$versus conversion plots up to ≈ 60% conversion ($\bar{M}_n$ ≈ 15.6 kg·mol^{-1}) as shown in Figure 8. In some cases, the $\bar{M}_n$s began to plateau at very high conversions indicating some irreversible termination reactions started to occur, particularly at higher *t*BMA initial concentrations – this is evident in Figure 7a) where some tailing is evident of some irreversible termination reactions. At higher AN initial concentrations such as that shown in Figure 7b) where $f_{AN,0}$ = 0.52, the tailing is not as evident as in Figure 7a). This is reasonable as there is more than sufficient AN to act as controller. Still, these results show NHS-BlocBuilder could be a successful controller for the methacrylate-rich copolymerizations using AN co-monomer without additional SG1, provided that there is sufficient co-monomer, in agreement with previous findings for glycidyl methacrylate-rich copolymerizations using S co-monomer.[34] Obviously, addition of free nitroxide would have helped improve the control of compositions with that much richer in the methacrylate ($f_{AN,0} < 0.2$).

Copolymer Compositions

For the S/AN copolymers initiated with NHS-BlocBuilder, the final molar composition of AN determined using FTIR shows that at low $f_{\mathrm{AN},0}$, the molar composition of AN was richer than that of the initial composition, while at high $f_{\mathrm{AN},0}$ ($f_{\mathrm{AN},0} > 0.50$) the copolymer composition became increasingly less rich in AN compared to the initial composition. A typical FTIR for a S/AN copolymerization with NHS-BlocBuilder is shown in Figure 9. In experiment ID S/AN-NHSBB-52, S/AN-NHSBB-70 and S/AN-NHSBB-86 (displayed in Table 3, with $f_{\mathrm{AN},0}$ = 0.52, 0.70 and 0.86, respectively), AN molar compositions, F_{AN}, of only 0.46, 0.50 and 0.52, respectively, were found in the final copolymers. As the suggested range of AN (F_{AN}) to reduce O_2 and CO_2 permeability in the S/AN copolymer is between 0.40 to 0.66 (25-50 wt% AN)[10], $f_{\mathrm{AN},0} > \approx 0.3$ (near the azeotropic composition) should be used to obtain an AN content in the S/AN copolymer that is sufficient for desired permeability.

The reactivity ratios for S/AN copolymerizations performed with NHS-BlocBuilder were found and compared to those we reported earlier for BlocBuilder/SG1 mediated S/AN copolymerization and for conventional radical copolymerization. For the BlocBuilder/SG1 initiated system, we found $r_{\mathrm{AN}} = 0.07 \pm 0.01$, $r_{\mathrm{S}} = 0.27 \pm 0.02$ using the Fineman-Ross method and $r_{\mathrm{AN}} = 0.10 \pm 0.01$, r_{S} = 0.2 8± 0.02 using the Kelen-Tüdos method.[27] In that same study, we extended the analysis to the Meyer-Lowry method for low conversion data (conversions = 0.073, 0.086 and 0.10) and to using direct numerical integration (i.e. error-in-variables method) for slightly higher conversion data (conversions = 0.10, 0.17 and 0.23). With 95% joint confidence intervals, we estimated

r_{AN} = 0.093-0.111 and r_S = 0.282-0.284 using the Meyer-Lowry and the direct numerical integration methods, respectively. For the NHS-BlocBuilder initiated system, reactivity ratios determined were r_{AN} = 0.025 ± 0.006, r_S = 0.37 ± 0.08 using the Fineman-Ross method, r_{AN} = 0.066 ± 0.018, r_S = 0.47 ± 0.06 using the Kelen-Tüdos and r_{AN} = 0.081 ± 0.046, r_S = 0.41 ± 0.09 using a non-linear least-squares fit of the Mayo equation.[57] By comparison, for conventional radical polymerization, r_{AN} = 0.04-0.06 and r_S = 0.47-0.54[58] and r_{AN} = 0.053 and r_S = 0.33.[59] Some have claimed that for RAFT-mediated S/AN copolymerizations with a dithioester chain transfer agent, the chain end has an effect on reactivity[60] but the same cannot be stated for our nitroxide-mediated systems as they both match fairly well to those values reported by conventional radical polymerization. Despite the slight discrepancy in the estimated reactivity ratios, both NMP systems studied by our group had similar azeotropic compositions, which were also in agreement with that observed for conventional radical polymerizations ($f_{AN} \approx 0.4$).[61,62]

FTIR was also 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 initial, while for $f_{AN,0} > 0.30$, the copolymer composition became increasingly less rich in AN compared to the initial composition. For example, in experiments *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 into the final copolymer. A similar compositional relationship was found previously for *t*BMA/AN copolymerization controlled by BlocBuilder/SG1.[27] Thus, the effect of the initiator did not significantly influence the incorporation of the monomers into the copolymer structure. Our previous analysis for tBMA/AN reactivity ratios suggested that replicates and more extensive design of experiments was necessary to obtain reliable estimates.[27] We still crudely estimated the reactivity ratios using Fineman-Ross and Kelen-Tüdös methods to obtain initial starting points for a more thorough analysis. The reactivity ratios for *t*BMA/AN copolymerizations using NHS-BlocBuilder were $r_{AN} = 0.08 \pm 0.01$, $r_{tBMA} = 1.28 \pm 0.15$ by the Fineman-Ross method and $r_{AN} = 0.14 \pm 0.03$ and $r_{tBMA} = 0.95 \pm 0.17$ by the Kelen-Tüdös method. These reactivity ratios were estimated from samples taken to low conversion (0.082-0.11). By comparison, the reactivity ratios for *t*BMA/AN copolymerizations using BlocBuilder/SG1 were $r_{AN} = 0.07 \pm 0.01$, $r_{tBMA} = 1.24 \pm 0.20$ by the Fineman-Ross method and $r_{AN} = 0.14 \pm 0.01$ and $r_{tBMA} = 0.89 \pm 0.19$ by the Kelen-Tüdös method.[27] The *t*BMA/AN reactivity ratios were not previously provided in the literature, but comparisons to similar alkyl methacrylate/AN copolymerizations by conventional radical methods are possible. For example, isobutyl methacrylate (*i*-BMA)/AN reactivity ratios by conventional radical copolymerization were $r_{AN} = 0.21$ and $r_{i\text{-}BMA} = 1.04$[61] while butyl methacrylate (BMA)/AN reactivity ratios were $r_{AN} = 0.30$ and $r_{BMA} = 1.08$[62] and $r_{AN} = 0.29$ and $r_{BMA} = 0.98$.[63] Thus, the *t*BMA/AN copolymerizations by BlocBuilder/SG1 or NHS-BlocBuilder yielded the same general reactivity ratio trend as alkyl methacrylate/AN systems copolymerized by conventional radical polymerization ($r_{AN} \approx 0.2\text{-}0.3$, $r_{methacrylate} \approx 1$).

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

An extension of the two binary systems studied above using NHS-BlocBuilder was to examine the ternary copolymerization of S, AN and *t*BMA in order to produce

S/AN copolymers with random placement of *t*BMA groups along the chain. The *tert*-butyl groups could later be cleaved to yield the acidic functionality. The appropriate monomer initial composition was selected to produce S/AN with sufficient random carboxylic acid functionality for reactive blending and acrylonitrile for barrier properties. A *t*BMA/S/AN terpolymer was synthesized using NHS-BlocBuilder initiator in a 50 wt% 1,4-dioxane solution at 90°C with $\bar{M}_{n,\,target}$ of 25 kg·mol^{-1} at complete conversion and monomer initial composition as follows: $f_{\mathrm{AN},0}$ = 0.50, $f_{S,0}$ = 0.40 and $f_{t\mathrm{BMA},0}$ = 0.10. The first-order kinetic plot of $ln(1\text{-}X)^{-1}$ versus time (Figure 10) exhibited a relatively linear trend up to ≈ 50 % conversion. The $\langle k_p \rangle [P\cdot]$ derived from the kinetic plot in Figure 10 gave 2.8 x 10^{-5} s^{-1}, which is in reasonable agreement for S/AN binary copolymerizations controlled by BlocBuilder/SG1 at the same temperature. This is not surprising as the terpolymerization was dominated by the S/AN monomers since only a low concentration of *t*BMA monomer in the initial composition was used ($f_{tBMA,0}$ = 0.10). Note that by fitting the best-fit line through the origin might suggest autoinitiation or autoacceleration effects were present. However, the molecular weight distributions remained narrow during the polymerization (Figure 11) and the M_n versus X plot in Figure 12 show that the early conversion samples had relatively higher M_ns for a given X relative to the theoretical line, which suggests some fractionation could have occurred.

GPC analysis of samples taken during the polymerization indicated that in all cases, the *t*BMA/S/AN terpolymer possessed narrow, monomodal molecular weight distributions with low $\bar{M}_w/\bar{M}_n$ between 1.10-1.19 during the course of the polymerization (Figure 11) and exhibited a linear M_n versus X plot up to about 50 %

conversion (Figure 12, $\bar{M}_n$ = 13.6 kg·mol^{-1}). Thus, NHS-BlocBuilder appeared 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 final molar composition according to ^{1}H NMR was $F_{t\text{BMA}}$ = 0.12, F_{S} = 0.67 and F_{AN} = 0.21. Thus, the final composition of *t*BMA in the copolymer nearly matched up with the initial composition of *t*BMA. Thus, there is sufficient concentration of the acid precursor for reactive blending purposes and close to a sufficient AN to provide satisfactory barrier properties, which suggests that a well-defined terpolymer can be accessed, after cleavage of the *t*BMA protecting group, for future reactive blending experiments with epoxy-functional PE, for example.

CONCLUSIONS

The succinimidyl ester terminated form of the alkoxyamine unimolecular initiator BlocBuilder, termed NHS-BlocBuilder, was an effective controller for the NMP of S/AN and *t*BMA/AN binary copolymerizations, with narrow monomodal molecular weight distributions ($\bar{M}_w/\bar{M}_n$= 1.14-1.26 for the S/AN copolymers and $\bar{M}_w/\bar{M}_n$= 1.23-1.50 for the *t*BMA/AN copolymers). Linear evolutions of $\bar{M}_n$ versus conversion X were observed for both series, up to $X \approx 0.6$. In particular, the tBMA/AN copolymerizations were relatively well-controlled (although possessing broader molecular weight distributions compared to the S/AN system) using NHS-BlocBuilder, without the addition of extra free SG1 nitroxide, which is typically required of methacrylate-rich copolymers using

BlocBuilder. Terpolymerizations of S/AN/*t*BMA (rich in S and AN) were also done using NHS-BlocBuilder and exhibited low $\overline{M}_w/\overline{M}_n$ =1.19 and linear $\overline{M}_n$ versus conversion X up to $X = 0.54$. The AN-containing co- and terpolymers revealed the ability of NHS-BlocBuilder to control a wide range of resins and serve as initial points for more sophisticated resin designs for AN-copolymer barrier materials.

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