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Routes to Carboxylic Acid Functional Acrylonitrile Copolymers via SG1-based Nitroxide Mediated Polymerization

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ABSTRACT

Styrene/acrylonitrile (S/AN) (AN feed compositions, $f_{\mathrm{AN},0}$ = 0.10-0.86) and *tert*-butyl methacrylate/AN (*t*BMA/AN) ($f_{\mathrm{AN},0}$ = 0.10-0.80) copolymers were synthesized at 90 °C in 50 wt% 1,4-dioxane solutions using unimolecular initiator *N*-(2-methylpropyl)-*N*-(1-diethylphosphono-2,2-dimethylpropyl)-*O*-(2-carboxylprop-2-yl) hydroxylamine (BlocBuilder) and in the case of the *t*BMA/AN copolymerizations, 8.0-8.5 mol% *N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) free nitroxide (SG1) relative to BlocBuilder was added. S/AN copolymers exhibited narrow, monomodal molecular weight distributions with low polydispersities (M_w/M_n = 1.14-1.26), and number average molecular weight (M_n) versus conversion (X) plots were relatively linear (M_n = 18.1 kg·mol^{-1}, $X \approx$ 0.7), suggesting “pseudo-living” behavior was approached. AN proved to be an effective controlling co-monomer for *t*BMA as *t*BMA/AN copolymers exhibited narrow monomodal molecular weight distributions with M_w/M_n = 1.17-1.50 and relatively linear M_n versus X plots to reasonably high conversion (M_n = 15.6 kg·mol^{-1}, $X \approx 0.6$). S/AN reactivity ratios were $r_{AN} = 0.07 \pm 0.01$, $r_S = 0.27 \pm 0.02$ (Fineman-Ross) and $r_{AN} = 0.07 \pm 0.01$, $r_S = 0.27 \pm 0.02$ (Kelen-Tüdos), in good agreement with conventional free radical polymerization. *t*BMA/AN reactivity ratios ($r_{AN} = 0.07 \pm 0.01$, $r_{tBMA} = 1.24 \pm 0.20$ (Fineman-Ross) and $r_{AN} = 0.14 \pm 0.01$, $r_{tBMA} = 0.89 \pm 0.19$ (Kelen-Tüdos)) were similar to those reported for related alkyl methacrylate/AN conventional radical copolymerizations.

Keywords: copolymerization; radical polymerization; polystyrene; nitroxide mediated polymerization; acrylonitrile

INTRODUCTION

Products such as gasoline and other pure or mixed hydrocarbon solvents, as well as gas molecules, can easily permeate polyethylene (PE) containers.[1] To overcome these permeability problems, appropriate polymer blending into PE is done to develop two-phase morphologies that act as barriers.[1-3] Many examples exist in the literature, such as blending nylon into the polyolefin, which has been suitably functionalized, so that the morphology is stabilized by *in situ* reaction during melt blending between appropriate functional groups between the nylon and the polyolefin.[2-10] This approach is limited to commercially available polymers with the inherent functionality from the polymerization process (nylon has terminal primary amine groups). To produce a more versatile range of barrier materials, it is desirable to include polymers where the functional group is not a direct residue of the original polymerization process such as is the case with nylon. 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.[11]

We aim to develop barrier polymers based on poly(styrene-*ran*-acrylonitrile) copolymers (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.[12] AN-based copolymers can have their microstructure easily controlled by controlled radical polymerization (CRP), which approaches the narrow molecular weight distribution and the ability to control microstructure typical of that of "living" or ionic polymerizations, without the need of air-free transfers, careful purification of reagents and functional group protection typically required of the latter.[13]

Nitroxide mediated polymerization (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., **Scheme 1**)[14]. There is significant literature concerning S/AN copolymerizations by CRP methods including RAFT[15,16], ATRP[17-19] and NMP[20-26]. Most studies have focused on S/AN feed compositions near the azeotropic composition (~ 60 mol% S) although several studies examined AN homopolymerization[27-31], particularly most recently using cobalt-mediated radical polymerization (CMRP).[32,33] S/AN has not been specifically copolymerized using BlocBuilder. This is relevant as BlocBuilder provides sufficient control of polymerization but with much faster polymerization rates compared to first-generation nitroxides such as 2,2 tetramethyl piperidine (TEMPO). Further, BlocBuilder has been able to control a wider range of monomers previously unattainable by TEMPO and to be effective at much lower temperatures. The study of BlocBuilder mediated S/AN compositions is of interest as commercially important S/AN copolymers can be accessed and combined with other monomers to form copolymers with a much wider latitude in properties. Further, AN, like styrene, is a suitable controlling co-monomer for methacrylate polymerizations via BlocBuilder.[34] Thus, AN not only serves to impart favorable barrier properties, but enables the BlocBuilder-controlled polymerization of methacrylic monomers.

We focused initially on carboxylic acid functional S/AN since many commercially PE resins are available with grafted epoxy functional glycidyl methacrylate, thus permitting blend stabilization with a carboxylic acid/epoxy reaction.[6] Such groups have been used in commercial blend systems[35] and can also be readily introduced into resins using CRP.[36] In particular, S/AN resins made from BlocBuilder are well-suited as they will have a carboxylic acid at the chain end from the initiator residue. Further, if desired, additional carboxylic acid groups can be introduced along the chain or in one block by incorporation of a carboxylic acid containing monomer, such as acrylic or methacrylic acid (and their protected forms such as *tert*-butyl acrylate or methacrylate).

Thus, we examine two families of resins with the goal of introducing carboxylic acids at the chain end or at random places along the chain into S/AN resins (**Scheme 2**). Placement of carboxylic acid groups on the chain end was done by S/AN copolymerizations with BlocBuilder. A wide range of S/AN compositions were thus studied to determine how much AN can be incorporated into the final copolymer. Random placement of the carboxylic acid was initially examined first by copolymerization of *tert*-butyl methacrylate (*t*BMA) with AN. *t*BMA was chosen for several reasons: i) it will not degrade the SG1 as the acidic form of the monomer would; ii) the methacrylate is not susceptible to back-biting chain transfer reactions as the acrylate is prone to.[37] Furthermore, we aimed to determine if AN was also an effective controller for *t*BMA over a wider range of AN feed compositions, as it has been for methyl methacrylate (MMA).[34] By studying these two binary copolymerizations, initial designs for AN-based barrier polymers can be proposed for suitable reactive blending with PE matrices.

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 (THF, 99.9%), dimethylformamide (DMF, HPLC grade 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. Poly(styrene) (PS, M_n = 13.0 kg·mol^{-1}, M_w/M_n = 1.10), poly(acrylonitrile) (PAN, M_n = 60.6 kg·mol^{-1}, M_w/M_n = 1.70), and poly(*t*BMA) (P*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.

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 only BlocBuilder as the nitroxide. 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 1. 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 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 (5.60 g, 0.0538 mol), acrylonitrile (1.22 g, 0.0230 mol) and 1,4-dioxane (6.80 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 $5°\text{C}\cdot\text{min}^{-1}$ 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. For the particular example, the final yield of S/AN-BB-30 after 240 minutes was 3.41 g (50% conversion based on gravimetry) with number-average molecular weight $M_\text{n} = 16.6\ \text{kg}\cdot\text{mol}^{-1}$ and polydispersity index $M_\text{w}/M_\text{n} = 1.17$ determined by gel permeation chromatography (GPC) calibrated relative to linear PMMA standards in DMF at 50ºC and corrected with composition-averaged Mark-Houwink parameters (see *Characterization* section for full details).

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

Nitroxide mediated copolymerizations of *t*BMA and AN in 50 wt% 1,4-dioxane solution were conducted at 90°C using BlocBuilder and additional free SG1 nitroxide. All copolymerizations were performed similarly to the S/AN copolymerizations. A 50 mL three-neck round bottom glass flask equipped with a magnetic stir bar, condenser and thermal well was used. The flask was set inside a heating mantle and placed on a magnetic stirrer. Formulations for initial molar feed compositions, $f_{\mathrm{AN},0}$, from 0.10-0.80 were followed and are found in Table 2. Target molecular weights at complete conversion ($M_{\mathrm{n},target}$), calculated based on the mass of *t*BMA and AN monomers relative to BlocBuilder or NHS-BlocBuilder initiator, were nearly 25 $\mathrm{kg \cdot mol^{-1}}$ for all experiments. For the *t*BMA/AN copolymerizations, 8.1-8.5 mol% SG1 free nitroxide relative to BlocBuilder was used to provide additional control for the polymerization. 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) and SG1 (0.008 g, 0.02 mmol) were added to the flask, which was then sealed with a rubber septum. *t*BMA (5.58 g, 0.0392 mol), AN (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 to 90°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 M_n = 10.4 kg·mol^{-1} M_w/M_n = 1.35 determined by GPC calibrated with linear poly(styrene) standards in THF at 40°C and corrected with composition-averaged Mark-Houwink parameters (see *Characterization* for full details).

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. DMF was used as the mobile phase for S/AN copolymers as the copolymers were not all fully soluble in THF. THF was used as the mobile phase for *t*BMA/AN copolymers since the copolymers were all soluble in THF. The eluent flow rate was 0.3 $mL \cdot min^{-1}$ during analysis. The GPC was also equipped with ultraviolet (UV 2487) and differential refractive index (RI 2410) detectors. The molecular weights were calibrated relative to linear, narrow molecular weight distribution PS standards (when using THF) and PMMA standards (when using DMF). The copolymer molecular weights were corrected using the Mark-Houwink relationship $[\eta] = KM^{\alpha}$, based on the following coefficients: $K_{\mathrm{PS}} = 11.4 \times 10^{-5}$ $dL \cdot g^{-1}$ and $\alpha_{\mathrm{PS}} = 0.716$ in THF at 40ºC[38] $K_{\mathrm{P}tBMA} = 11.2 \times 10^{-5}$ $dL \cdot g^{-1}$ and $\alpha_{\mathrm{P}tBMA} = 0.692$ in THF at 30ºC[39]; $K_{\mathrm{PAN}} = 21.2 \times 10^{-5}$ $dL \cdot g^{-1}$ and $\alpha_{\mathrm{PAN}} = 0.75$ in DMF at 60ºC (data at 50ºC was not available);[40] while S/AN copolymers in DMF at various AN compositions (F_{AN}) were also used to estimate S/AN copolymer molecular weights: $K_{\mathrm{SAN}} = 1.62 \times 10^{-4}$ $dL \cdot g^{-1}$ and $\alpha_{\mathrm{SAN}} = 0.75$ ($F_{AN} = 0.40$, T = 30 ºC)[41] and $K_{\mathrm{SAN}} = 1.2 \times 10^{-4}$ $dL \cdot g^{-1}$ and $\alpha_{\mathrm{SAN}} = 0.77$ ($F_{AN} = 0.626$, T = 30 ºC).[42] For the PMMA standards used in DMF, $K_{\mathrm{PMMA}} = 2.07 \times 10^{-5}$ $dL \cdot g^{-1}$ and $\alpha_{\mathrm{PMMA}} = 0.632$ in DMF at 50ºC.[45] The molecular weights were corrected by compositionally averaging the Mark-Houwink coefficients for the copolymers and then correcting appropriately against the PMMA standards for the S/AN copolymers and against the PS 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 $\mathrm{cm^{-1}}$, 2200 $\mathrm{cm^{-1}}$, 1200 $\mathrm{cm^{-1}}$ 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 the PS, PAN and P*t*BMA standards. All reactivity ratio determinations were done using samples that were polymerized to low conversion (<10%) to avoid compositional drift corrections.

RESULTS AND DISCUSSION

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

The unimolecular initiator, BlocBuilder (structure shown in **Scheme 1**) 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. 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}, > 0.40-0.66 provides better barrier properties.[12] Various S/AN mixtures were synthesized via NMP with BlocBuilder, using our previous experience with S polymerizations by NMP as a guide.[44,45] At 90 °C in 50 wt%

1,4-dioxane solution, S/AN mixtures up to an AN molar feed concentration, $f_{\mathrm{AN},0}$ = 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 1** representing the semi-logarithmic plot of scaled conversion ($ln(1\text{-}X)^{-1}$ where X = monomer conversion) versus time. Note that the apparent rate constant, obtained from the slope in the linear range of **Figure 1**, $\langle \boldsymbol{k_p} \rangle$ [P$^{\cdot}$], (where $\langle \boldsymbol{k_p} \rangle$ is the average propagation rate constant for the copolymerization and [P$^{\cdot}$] is the concentration of propagating radicals), decreased slightly from (5.2 ± 0.8) × 10^{-5} to (3.0 ± 0.2) × 10^{-5} s^{-1} with increasing feed composition ($f_{\mathrm{AN},0}$ = 0.10-0.70). This is reasonable as recently published data for the homopropagation rate constant, k_p, of AN ($k_{p,\ AN}$ = 1.1 × 10^4 L mol^{-1} s^{-1})[46] suggests it is nearly an order of magnitude higher compared to the homopropagation rate constant for styrene ($k_{p,S}$ = 1.8 × 10^3 L mol^{-1} s^{-1}) at 90 °C.[47] However, the equilibrium constant K between the dormant and active SG1-capped chains are not dissimilar, based on literature estimates. For styrene homopolymerizations, K_S = 4 x 10^{-10} mol L^{-1} at 90 °C[48] while Nicolas et al. used the K for n-butyl acrylate[48] to estimate K for acrylonitrile as K_{AN} = 1 x 10^{-11} mol L^{-1}.[34]

The combination of $\langle \boldsymbol{k_p} \rangle$, and the average K, $\langle \boldsymbol{K} \rangle$, for the S/AN copolymerizations suggests that they offset each other and this combined effect can be neatly summarized by the following equations to predict $\langle k_p \rangle$[P·] from literature data. Kinetics for free radical polymerizations are often best described by penultimate kinetic models and sufficient data is available for S/AN conventional radical copolymerizations to make reasonable predictions. The $\langle k_p \rangle$ based on the implicit penultimate model is given by[49]:

$$\langle k_p \rangle = \frac{r_{AN} f_{AN}^2 + 2 f_{AN} f_S + r_S f_s^2}{r_{AN} \dfrac{f_{AN}}{\overline{k_{p,AN}}} + r_S \dfrac{f_S}{\overline{k_{p,S}}}} \qquad [1]$$

where:

$$\overline{k_{p,AN}} = k_{p,AN} \frac{r_{AN} f_{AN} + f_S}{r_{AN} f_{AN} + \dfrac{f_S}{s_{AN}}}; \quad \overline{k_{p,S}} = k_{p,S} \frac{r_S f_S + f_{AN}}{r_S f_S + \dfrac{f_{AN}}{s_S}}. \qquad [2]$$

Note that the monomer reactivity ratios for AN and S are given by r_{AN} and r_S, respectively, while the radical reactivity ratios for AN and S are given by s_{AN} and s_S, respectively. The molar feed fractions for AN and S are given by f_{AN} and $f_S = 1 - f_{AN}$, respectively. The concentration of propagating macroradicals for a system controlled by persistent free radicals like SG1 is given by Fischer's expression[50]:

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

In Equation [3], $[I]_0$ is the initial concentration of the BlocBuilder nitroxide initiator, $\langle k_t \rangle$ is the average termination rate constant, *t* is the time and $\langle K \rangle$is the average equilibrium constant for the implicit penultimate model derived by Charleux and co-workers.[51]

$$\langle K \rangle = \frac{\dfrac{r_{AN} f_{AN}}{k_{p,AN}} + \dfrac{r_S f_S}{k_{p,S}}}{\dfrac{r_{AN} f_{AN}}{k_{p,AN} K_{AN}} + \dfrac{r_S f_S}{k_{p,S} K_S}} \qquad [4]$$

The $\langle k_t \rangle$ for the penultimate copolymerization model is given by[52]:

$$\langle k_t \rangle = \left(p_S k_{t,S}^{1/2} + p_{AN} k_{t,AN}^{1/2} \right)^2 \qquad [5]$$

where $k_{t,S}$ and $k_{t,AN}$ are the homo-termination rate constants for S and AN, respectively while p_S and p_{AN} are given by:

$$p_S = \frac{\dfrac{r_S f_S}{k_{p,S}}}{\dfrac{r_S f_S}{k_{p,S}} + \dfrac{r_{AN} f_{AN}}{k_{p,AN}}} \text{and } p_{AN} = 1 - p_S. \qquad [6].$$

The $k_{t,S}$ at 90 °C is taken from Beuermann and Buback[53] to be 1.3×10^8 L mol^{-1} s^{-1} while $k_{t,AN}$ is taken from the expression provided by Keramopoulos and Kiparissides[54] with $k_{t,AN} = 1.98x10^{14} e^{-5400/RT}$ (*R* = gas constant, *T* = temperature [=] K) to give $k_{t,AN}$ (90 °C) = 9.2×10^9 L mol^{-1} s^{-1}. The only other parameters required are the monomer and radical reactivity ratios for the penultimate model which are taken from Hill et al from data at 60 °C (since data at 90 °C was not available)[55]:

$r_S = 0.22$, $r_{AN} = 0.039$, $s_S = 0.634$ and $s_{AN} = 0.229$. Given this literature data and the expressions above, a predicted $\left\langle \boldsymbol{k_p} \right\rangle$[P·] for S/AN nitroxide mediated copolymerization can be compared to the experimental data. Note that [P·] was estimated as steady-state was approached, typically after a polymerization time ~ 5 x 10^2 s^{-1} where the change in [P·] is negligible. The experimental results and the predicted apparent rate constants are plotted as a function of f_S in **Figure 2**. Note that the predicted data does not match very closely the experimental data but in either case the variation of $\left\langle \boldsymbol{k_p} \right\rangle$[P·] with composition was not wide.

The molecular weights obtained via GPC were used in conjunction with the kinetic data to obtain plots of number average molecular weight (M_n) versus conversion (X). Such plots are used to evaluate the control of the polymerization for CRP processes, particularly to see if the polymerization approaches the linear behavior indicative of truly "living" polymerizations. The copolymers exhibited narrow molecular weight distributions and appeared monomodal in nature (**Figure 3**) with low polydispersities (M_w/M_n = 1.17-1.26), suggestive of controlled polymerizations. **Figure 4** shows the plot of M_n versus X for BlocBuilder controlled S/AN copolymerizations at various $f_{AN,0}$. Note that the straight, solid line is the theoretically expected M_n versus X behavior. Note that there was some uncertainty in estimation of M_n since the corrections may not have available at the temperature used for the GPC. Still, the plots were relatively linear up to ≈ 40% conversion ($M_n \approx 16.0$ kg·mol^{-1}) suggesting that a "pseudo-living" behavior was approached up to that point. The characteristics of the final S/AN copolymers controlled with BlocBuilder are displayed in **Table 3**.

Kinetics of tert-Butyl Methacrylate/Acrylonitrile Random Copolymers (poly(tBMA/AN)) Using BlocBuilder Initiator

Prior to synthesizing S/AN copolymers with COOH functionality at random locations along the chain length, 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. *t*BMA/S copolymers synthesized using BlocBuilder were reported by our research group[45] at the same conditions described in our study here. The previous section of this manuscript explored S/AN copolymerization using the carboxylic acid terminated BlocBuilder initiator. The results here with *t*BMA/AN would complete the examination of the three binary NMP systems that would be relevant for subsequent tailoring of terpolymers for functional S/AN-based barrier materials with random methacrylic acid groups.

*t*BMA/AN copolymers were synthesized using BlocBuilder initiator with an excess of SG1 (8.1-8.5 mol% SG1 relative to BlocBuilder) for $f_{AN,0}$ from 0.11-0.80 in 50 wt% dioxane solutions at 90ºC. The excess of SG1 free nitroxide was used to provide sufficient concentration of the persistent radical to control the methacrylate-rich polymerization.[34,44,45,51,56] **Figure 5** shows the first-order kinetic plots of $ln(1-X)^{-1}$ versus time for *t*BMA/AN copolymerizations with

BlocBuilder/SG1. For all plots, conversion increased with a relatively linear trend up to ≈ 50% scaled conversion (depending on the AN feed composition), implying a constant radical concentration and suggests a controlled polymerization. Extraction of the apparent rate constants, $\langle k_p \rangle$[P·], from the slopes indicated that increasing AN feed concentration tended to decrease the polymerization rate from (3.3 ± 0.5) × 10^{-5} to (5.1 ± 0.3) × 10^{-6} s^{-1}. In the case of using excess SG1 free nitroxide, the $\langle k_p \rangle$[P·] values can be converted into the product of $\langle k_p \rangle \langle K \rangle$, which combines the two key features controlling the NMP process. Given the definition of $\langle K \rangle$ as the ratio of the concentration of active species ([P·] and concentration of free nitroxide [SG1]) to that of the dormant species (concentration of SG1-capped macroradicals [P-SG1]), $\langle k_p \rangle \langle K \rangle$ can be written as Equation [7] provided some assumptions are applied.

$$\langle k_p \rangle \langle K \rangle = \langle k_p \rangle \frac{[SG1][P\cdot]}{[P-SG1]} \approx \langle k_p \rangle \frac{[SG1]_0[P\cdot]}{[BlocBuilder]_0} = \langle k_p \rangle [P\cdot] r \qquad [7]$$

First, it is assumed that [SG1] is added at sufficiently high concentration that it does not vary much during the course of polymerization so that [SG1] ≈ initial SG1 concentration $[SG1]_0$. Also, [P-SG1] ≈ $[BlocBuilder]_0$ if the chains remain relatively pseudo-living, which holds approximately true during the early stages of the polymerization where the $\ln[(1-X)^{-1}]$ versus time plots were linear. This was later further verified by the linear M_n versus X plots for the copolymerization in the X ranges studied. Given these assumptions, Equation [7] can be written with $\langle k_p \rangle \langle K \rangle$ as a function of the $\langle k_p \rangle$[P·] values from the slopes of the kinetic plots in **Figure 5** and the molar concentration ratio of initial free nitroxide to BlocBuilder given as $r = [SG1]_0 / [BlocBuilder]_0$.

The experimental estimates of $\langle k_p \rangle \langle K \rangle$ for the *t*BMA/AN copolymerizations are plotted as a function of $f_{AN,0}$ in **Figure 6**. Unlike the S/AN copolymerization described in the previous section, the $\langle k_p \rangle \langle K \rangle$ drops much more steeply with increasing AN content in the feed. As noted previously, Junkers et al. [46] recently reported data for $k_{p,AN} = 1.1 \times 10^4$ L mol^{-1} s^{-1}, implying it is between half to one order magnitude higher compared to the homopropagation rate constant of *t*BMA ($k_{p,tBMA} = 1.6 \times 10^3$ L mol^{-1} s^{-1}) at 90 °C[57]. However, there is a larger discrepancy between the equilibrium constants of the two species. Nicolas et al. took $K_{AN} \approx K_{BA} = 1 \times 10^{-11}$ mol L^{-1}.[34] The equilibrium constant for *t*BMA has not been measured but it was estimated to be similar to the structurally related MMA ($K_{tBMA} \approx 2.6 \times 10^{-7}$ mol L^{-1}).[45]

Since data required for the *t*BMA/AN copolymerization is scarce and the only reactivity ratios known for this particular pair are those derived from our study ($r_{AN} = 0.14 \pm 0.03$ and $r_{tBMA} = 0.89 \pm 0.19$), the predicted $\langle k_p \rangle \langle K \rangle$ for the *t*BMA/AN assumed a terminal model for the kinetics and the expression derived by Charleux and co-workers for such a model was subsequently used to compare against our experimental data[51].

$$\langle k_p \rangle \langle K \rangle = \frac{r_{AN} f_{AN}^2 + 2 f_{AN} f_{tBMA} + r_{tBMA} f_{tBMA}^2}{r_{AN} \dfrac{f_{AN}}{k_{p,AN} K_{AN}} + r_{tBMA} \dfrac{f_{tBMA}}{k_{p,tBMA} K_{tBMA}}} \qquad [8]$$

Note that the feed fractions for AN and *t*BMA are given by f_{AN} and f_{tBMA}, respectively, in Equation [8]. In **Figure 6**, there is reasonable agreement between the experimental data and the predicted $\langle k_p \rangle \langle K \rangle$ in the feed composition range studied. More rigorous testing of the model would require examination of much lower AN feed compositions, where there is a dramatic increase in $\langle k_p \rangle \langle K \rangle$ expected. However, our motivation is focused towards using higher AN feed compositions since we ultimately desire to use AN to impart more favorable barrier properties.

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: *tBMA*/AN-BB/SG1-80 in **Table 2** and **Table 4**) the samples were easily soluble in THF. Note that Mark-Houwink parameters were not available for poly(AN) in THF, so the corrections were not ideal. However, GPC analysis for *t*BMA/AN experiments revealed 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 7** display a leftward shift in the molecular weight distribution, indicating a steady, monomodal growth in the copolymer chains over time. M_n versus X plots

(**Figure 8**) were linear up to ≈ 55 % conversion (M_n = 14.8 kg·mol^{-1}) for the different AN feed compositions, indicating pseudo-living behavior was approached up to that point. In some cases, the M_ns 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 4**.

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 equation[58]shown in Equation [9] which requires the knowledge of the monomer reactivity ratios[59-61] 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).

$$F_1 = \frac{r_1 f_1^2 + f_1(1-f_1)}{r_2(1-f_1)^2 + 2f_1(1-f_1) + r_1 f_1^2} \qquad (9)$$

The copolymer compositions were predicted in terms of the initial monomer concentrations using Mayo's terminal copolymerization model[58] assuming the active site reactivity depends on the nature of the reactive terminus. Monomer reactivity ratios for S/AN and *t*BMA/AN were also fit using the Kelen-Tüdos method.[60,61]

For conventional radical polymerization, reactivity ratios 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. For example, Fan et al. reported r_{AN} = 0.19 and r_S = 0.46 for S/AN copolymerization by RAFT, which were slightly higher than that reported by conventional radical polymerization. They attributed the difference to the different affinity of the propagating chain end with the dithioester chain transfer agent used.[16] The reactivity ratios for S/AN copolymerizations using BlocBuilder were r_{AN} = 0.07 ± 0.01 and r_S = 0.27 ± 0.02 by the Finemann-Ross method and r_{AN} = 0.10 ± 0.01 and r_S = 0.28 ± 0.02 by the Kelen-Tüdos method. Conventional radical copolymerization of S/AN provided reactivity ratios of r_{AN} = 0.04-0.06 and r_S = 0.47-0.54[62] and r_{AN} = 0.053 and r_S = 0.331.[55] Thus, the reactivity ratios determined by us are closer to that reported by conventional radical polymerization than that reported by Fan et al[19], suggesting that the activity of the chain end was not as strongly altered by the nitroxide as it was by the dithioester. Thee reactivity ratios are summarized in the Mayo plots shown in **Figure 9**, which indicate the copolymer composition expected for a given feed. Note that the azeotropic composition at about 40 mol% AN was still attained, which is in agreement with previous studies.

*t*BMA/AN reactivity ratios for BlocBuilder/SG1 controlled polymerizations were r_{AN} = 0.07 ± 0.01 and r_{tBMA} = 1.24 ± 0.20 (Fineman-Ross) method and r_{AN} = 0.14 ± 0.03 and r_{tBMA} = 0.89 ± 0.19 (Kelen-Tüdos). *t*BMA/AN reactivity ratios were not available from the literature and are thus compared to similar methacrylate/AN systems. For example, Nair and Muthana reported isobutyl methacrylate (i-BMA)/AN reactivity ratios by conventional radical copolymerization of r_{AN} = 0.21 and $r_{i\text{-}BMA}$ = 1.04 and butyl methacrylate (BMA)/AN reactivity ratios of r_{AN} = 0.30 and r_{BMA} = 1.08[63] while Kapur and Brar reported r_{AN} = 0.30 and r_{BMA} = 1.08[64] and Greenley reported r_{AN} = 0.29 and r_{BMA} = 0.98.[65] Khesareh et al. reported MMA/AN reactivity ratios of r_{AN} = 0.15 and r_{MMA} = 1.04[66] while El-Sabee et al. reported ethyl methacrylate (EMA)/AN reactivity ratios from conventional radical polymerization of r_{AN} = 0.34 ± 0.01 and r_{EMA} = 0.85 ± 0.12.[67] Thus, the *t*BMA/AN reactivity ratios agree reasonably well with those reported by conventional radical polymerization of related alkyl methacrylate/AN copolymerizations. **Figure 10** shows the Mayo plot for the *t*BMA/AN system studied here and it implies that it was quite difficult to obtain *t*BMA/AN copolymer rich in AN as the feed concentration of AN was increased.

CONCLUSION

S/AN resins ($f_{\mathrm{AN},0}$ = 0.10-0.86) were synthesized using BlocBuilder unimolecular initiator at 90 °C in a controlled manner with narrow molecular weight distribution ($M_\mathrm{w}/M_\mathrm{n}$ = 1.14-1.26) and relatively linear M_n versus conversion plots (M_n = 15.3-18.1 kg·mol^{-1}, X = 40-70%). The incorporation of AN into styrenic resins has been possible at relatively high loadings, in some cases up to ≈ 52 mol%. AN containing resins with potential random carboxylic acid functionality were derived by using the protected form of methacrylic acid, *t*BMA, in a copolymerization with AN with BlocBuilder/SG1 at 90 °C. For $f_{\mathrm{AN},0}$ = 0.10-0.80, *t*BMA/AN copolymers exhibited relatively narrow molecular weight distribution ($M_\mathrm{w}/M_\mathrm{n}$ = 1.17-1.40) and linear M_n versus conversion plots (M_n = 14.8 kg·mol^{-1}, X = 55 %). The reactivity ratios were $r_{AN} = 0.07 \pm 0.01$, $r_S = 0.27 \pm 0.02$ (Fineman-Ross) and $r_{AN} = 0.10 \pm 0.01$, $r_S = 0.28 \pm 0.02$ (Kelen-Tüdos) for S/AN copolymerizations, in good agreement with conventional radical polymerizations. For *t*BMA/AN copolymerizations, $r_{AN} = 0.07 \pm 0.01$, $r_{tBMA} = 1.24 \pm 0.20$ (Fineman-Ross) and $r_{AN} = 0.14 \pm 0.03$, $r_{tBMA} = 0.89 \pm 0.19$ (Kelen-Tüdos), which were similar to related alkyl methacrylate/AN conventional radical copolymerizations. These results suggest terminal and pendant carboxylic acid functional acrylonitrile copolymers can be synthesized in a controlled manner using BlocBuilder type unimolecular initiators.

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