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One-Step Poly(styrene-*alt*-maleic anhydride)-*block*-poly(styrene) Copolymers with Highly Alternating Styrene/Maleic Anhydride Sequences Are Possible by Nitroxide-Mediated Polymerization

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ABSTRACT: Styrene/maleic anhydride (S/MA) copolymerizations at initial molar MA feed concentrations $f_{MA,0} = 0.10-0.55$ were done at 80−110 °C in 50 wt % 1,4-dioxane using 5 mol % {*tert*-butyl-[1-(diethoxy-phosphoryl)-2,2-dimethylpropyl]amino}oxidanyl (SG1) relative to -2-({*tert*-butyl-[1-(diethoxyphosphoryl)-2,2-(dimethylpropyl)amino}oxy)-2-methylpropionic acid (BlocBuilder). As $f_{MA,0}$ increased, the apparent rate constants increased dramatically. Copolymerizations performed with nearly equimolar feeds $f_{MA,0} = 0.45-0.55$ at 110 °C had apparent rate constants ~20 times that of styrene at the same temperature. S/MA copolymerizations performed at 110 °C with practically equimolar feeds resulted in nearly alternating S/MA/S structures while those performed with $f_{MA,0} = 0.1-0.4$ possessed little to no S/MA/S alternating structures as indicated by ^{13}C NMR spectroscopy. However, NMP of S/MA done at 90 °C with a styrene-rich feed composition ($f_{MA,0} = 0.2$) resulted in a poly(S-*alt*-MA)-*block*-poly(S) diblock in a single step. ^{13}C NMR revealed two significant populations of triads corresponding to S/MA/S alternating sequences and to S/S/S homopoly(styrene) sequences. BlocBuilder enabled the polymerization of these one-step block copolymers with a strictly alternating S/MA first block by NMP, thus permitting NMP to join reversible addition−fragmentation transfer polymerization as another controlled radical polymerization method to attain alternating S/MA microstructures.

Introduction

Styrene/maleic anhydride (S/MA) copolymers are widely used as polymer blend compatibilizers and adhesion promoters.[1−6] Such copolymers are generally prepared by conventional free radical polymerization and are characterized by relatively broad molecular weight distributions with polydispersities $\bar{M}_w/\bar{M}_n \sim 2$. More recently, however, the advent of controlled radical polymerization (CRP) has enabled the possibility of producing resins with much lower $\bar{M}_w/\bar{M}_n < 1.5$ and greater control of architecture (e.g., ability to form block copolymers) compared to conventional radical polymerization.[7] CRP methods such as nitroxide-mediated polymerization (NMP)[8−10] and reversible addition−fragmentation transfer polymerization (RAFT)[11−14] have been applied toward producing S/MA copolymers with $\bar{M}_w/\bar{M}_n < 1.5$. Further, due to the alternating structures possible for the S and electron accepting MA pair, poly(S-*alt*-MA)-*b*-poly(S) block copolymers could be potentially prepared in a single step under proper conditions.[8] Such functionalized block copolymers would be highly useful as surfactants and as possible precursors for in situ formation of melt-processed block copolymers or composites with nanometer scale morphologies.

Among the CRP methods, RAFT technologies have generally been favored for precisely alternating S/MA copolymers due to the relatively low temperatures (≈80 °C) required to obtain strictly alternating monomer sequences.[13] Initially, with earlier generation nitroxides such as 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) and α-hydrido-based alkoxyamines as the stable free radical mediator/initiators, NMP required much higher reaction temperatures (≈120 °C).[8−10] Recently, unimolecular initiators based on the SG1 family of nitroxides such as 2-({*tert*-butyl-[1-(diethoxyphosphoryl)-2,2-dimethylpropyl]amino}oxy)-2-methylpropanoic acid (BlocBuilder, Arkema) have been able to polymerize in a controlled fashion not only styrenics and acrylates[15−17] but also methacrylates[18−21] (with a small fraction of suitable comonomer) at temperatures as low as 90 °C. Thus, it should be possible for BlocBuilder-controlled NMP to produce nearly alternating S/MA copolymers at temperatures closely approaching that employed by RAFT methodologies. The following study will attempt to characterize the S/MA NMP polymerization with BlocBuilder as a function of feed composition, additional SG1 free nitroxide, monomer concentration, and reaction temperature to determine the utility of NMP in producing such technologically relevant alternating copolymers and block copolymers.

Experimental Section

Materials. Styrene (99%), calcium hydride (90−95%, reagent grade), and basic alumina (Brockmann, Type I, 150 mesh) were obtained from Aldrich. Maleic anhydride (MA) (99%) was obtained from Fluka. 1,4-Dioxane (99.5%), tetrahydrofuran (99.5%), and methanol (99.8%) were obtained from Caledon Laboratories. 2-({*tert*-Butyl[1-(diethoxyphosphoryl)-2,2-dimethylpropyl]amino}oxy)-2-methylpropanoic acid, also known as BlocBuilder (99%), was acquired from Arkema and used without further purification. {*tert*-Butyl[1-(diethoxyphosphoryl)-2,2-dimethylpropyl]amino}oxidanyl, also known as SG1 (>85%), was kindly donated by Noah Macy of Arkema and used as received. Styrene was used after purifying by passage through a column of calcium hydride/basic alumina (5 wt %

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calcium hydride), sealed in a flask under a head of nitrogen, and stored in a refrigerator until required. All other reagents were used as received.

Synthesis of Styrene/Maleic Anhydride Copolymers. All polymerizations were performed in a 100 mL three-neck round-bottom glass flask equipped with a condenser, thermal well, and a magnetic Teflon stir bar. The flask was placed inside a heating mantle, and the equipment was placed on a magnetic stirrer. Table 1 lists all the formulations studied. All polymerizations used a target number-average molecular weight ($\bar{M}_n$) at complete conversion of 25 kg mol^{-1}. A specific formulation for an initial feed composition of MA ($f_{MA,0}$) equal to 0.10 is given as an example (SMA-1, Table 1). Maleic anhydride (MA) (1.51 g, 15.4 mmol), BlocBuilder (0.24 g, 0.63 mmol), SG1 (0.009 g, 0.03 mmol, 5 mol % relative to BlocBuilder), and 1,4-dioxane solvent (15.87 g, 181 mmol) were added to the reactor, and mixing commenced with the stir bar. A thermocouple was inserted through one of the reactor ports via a temperature well and connected to a controller. To another neck, the condenser was connected. The condenser was capped with a rubber septum with a needle inserted to relieve the pressure of the nitrogen purge applied during the reaction. The condenser was connected to a chilling unit (Neslab 740) that used a 50 vol % glycol/water mixture to prevent loss of the monomers and solvent due to evaporation. The chiller was set to 5 °C. The third port was sealed with a septum and used as the sampling port. The reactor was sealed, and a nitrogen purge was applied while dissolving the MA in the solvent. Then, previously purified styrene (14.47 g, 139 mmol) was injected into the reactor via a syringe, and the nitrogen purge was continued. Purging at ambient conditions was continued for 30 min after the styrene was added. The reactor was then heated to the appropriate temperature (110 °C in this case) at a rate of about 10 °C min^{-1} while maintaining a nitrogen purge. The initial polymerization time was taken when the reactor temperature reached 105 °C. Samples were taken with a syringe periodically until the samples became too viscous to withdraw. Polymers from the samples taken were precipitated with methanol. For the specific example cited, the polymerization was stopped after 1 h. After precipitation, the crude polymer was redissolved in 1,4-dioxane and precipitated once more into methanol to remove the unreacted MA more effectively. After precipitation, the samples were dried overnight in a vacuum oven at 70 °C to remove any additional solvent or unreacted monomer. For the specific example cited, the final yield was 8.4 g (54% conversion) with $\bar{M}_n = 12.1$ kg mol^{-1} and polydispersity index $\bar{M}_w/\bar{M}_n = 1.18$ as determined by gel permeation chromatography (GPC) calibrated relative to linear poly(styrene) standards with THF as the eluent at 40 °C. The molar composition of the final copolymer sample with respect to MA, F_{MA}, was 0.15 as determined by ^{13}C nuclear magnetic resonance (NMR). All final copolymer characteristics can be found in Table 2.

Table 1. Styrene/Maleic Anhydride Copolymerization Kinetics Experiments

experiment ID[a]	$f_{MA,0}$[b]	$[MA]_0$ (mol L^{-1})	$[S]_0$ (mol L^{-1})	r[c]	T (°C)	$\langle k_p \rangle \langle K \rangle$[d] (s^{-1})
SMA-1	0.100	0.5	4.2	0.048	110	$(1.0 \pm 0.1) \times 10^{-5}$
SMA-2	0.198	0.9	3.8	0.049	110	$(9.6 \pm 1.7) \times 10^{-6}$
SMA-3	0.298	1.4	3.4	0.054	110	$(2.4 \pm 0.4) \times 10^{-5}$
SMA-4	0.398	1.9	2.9	0.043	110	$(2.2 \pm 0.4) \times 10^{-5}$
SMA-4.5	0.447	2.2	2.7	0.050	110	$(8.7 \pm 1.0) \times 10^{-5}$
SMA-5	0.489	2.4	2.5	0.054	110	$(9.6 \pm 0.2) \times 10^{-5}$
SMA-5.5	0.556	2.8	2.2	0.051	110	$(8.6 \pm 1.0) \times 10^{-5}$
SMA-6	0.490	2.4	2.5	0.054	90	$(7.3 \pm 0.9) \times 10^{-6}$
SMA-7	0.489	2.4	2.5	0.053	80	$(5.3 \pm 0.8) \times 10^{-6}$
SMA-8	0.486	2.4	2.5	0.049	100	$(9.6 \pm 1.5) \times 10^{-5}$
SMA-9	0.483	2.4	2.5	0.10	110	$(1.2 \pm 0.3) \times 10^{-4}$
SMA-10	0.489	1.6	1.7	0.10	110	$(7.2 \pm 0.4) \times 10^{-5}$
SMA-11	0.204	1.0	3.7	0.054	90	$(1.2 \pm 0.2) \times 10^{-5}$

[a] Experimental identification (ID) is given by SMA-X where SMA = styrene (S) and maleic anhydride (MA) and the number abbreviation refers to the experiment number. [b] $f_{MA,0}$ is the initial molar feed composition of maleic anhydride, and F_{MA} is the final molar feed composition of maleic anhydride in copolymer determined using ^{13}C NMR. [c] Initial molar concentration ratio of SG1 free nitroxide to BlocBuilder initiator = r = $[SG1]_0/[BlocBuilder]_0$. [d] $\langle k_p \rangle$ is the average propagation rate constant, and $\langle K \rangle$ is the average equilibrium constant. The error bars for the $\langle k_p \rangle$ and $\langle K \rangle$ are derived from the standard errors for the slopes from the kinetic plots shown in Figure 1a,c.

Synthesis of Poly(maleic anhydride-*alternating*-styrene)-*block*-poly(styrene) (P(MA-*alt*-S)-*b*-PS) Block Copolymer. An identical reactor setup was used for the synthesis of P(MA-*alt*-S)-PS as the previously mentioned copolymerization. The macroinitiator (SMA-5, 0.50 g, 0.03 mmol), styrene (4.72 g, 45.4 mmol), and 1,4-dioxane (8 mL) were added to the reactor, which was than sealed. The mixture was bubbled with nitrogen for 30 min before the reactor was heated to 115 °C. A purge of nitrogen was maintained throughout the polymerization, which was carried out for 72 min (t_0 was taken when $T = 110$ °C) while taking samples periodically. The samples and final copolymers were precipitated in methanol, filtered, and dried in a vacuum oven at 60 °C overnight. A yield of 1.5 g (29%) was recovered with $\bar{M}_w/\bar{M}_n = 1.60$, $\bar{M}_n = 35.3$ kg mol^{-1}, and $F_{MA} = 0.05$.

Characterization. The overall monomer conversion was determined by gravimetry. The molecular weight distribution was

Table 2. Molecular Weight and Composition Characterization of Styrene/Maleic Anhydride Copolymers

experiment ID[a]	$f_{MA,0}$[b]	r[c]	T (°C)	t_{polym} (min)	X[c]	F_{MA}[b]	$\bar{M}_n$[d] (kg mol^{-1})	$\bar{M}_w/\bar{M}_n$[d]
SMA-1	0.100	0.048	110	120	0.54	0.15	12.1	1.18
SMA-2	0.198	0.049	110	155	0.67	0.28	19.1	1.23
SMA-3	0.298	0.054	110	45	0.74	0.39	14.1	1.28
SMA-4	0.398	0.043	110	25	0.53	0.43	15.0	1.27
SMA-4.5	0.447	0.050	110	12	0.65		15.4	1.33
SMA-5	0.489	0.054	110	9	0.70	0.48	15.5	1.31
SMA-5.5	0.556	0.051	110	6	0.72		13.3	1.22
SMA-6	0.490	0.054	90	30	0.23	0.48	17.6	1.32
SMA-7	0.489	0.053	80	90	0.39	0.47	10.6	1.39
SMA-8	0.486	0.049	100	12	0.76	0.47	16.6	1.28
SMA-9	0.483	0.103	110	12	0.61	0.47	16.1	1.27
SMA-10	0.489	0.102	110	30	0.74	0.50	12.8	1.28
SMA-11	0.204	0.054	90	130	0.56	0.30	6.4	1.61
SMA-5-PS	0.48	-	115	72	0.31	0.05	35.3	1.60

[a] Experimental identification (ID) is given by SMA-X, where SMA = styrene (S) and maleic anhydride (MA) and the number abbreviation refers to the experiment number. SMA-5−PS is a chain extension of styrene using SMA-5 as a macroinitiator (PS refers to poly(styrene)). [b] $f_{MA,0}$ is the initial molar feed composition of maleic anhydride, and F_{MA} is the final molar feed composition of maleic anhydride determined using ^{13}C NMR. [c] Initial molar concentration ratio of SG1 free nitroxide to BlocBuilder initiator = r = $[SG1]_0/[BlocBuilder]_0$. X is the conversion determined gravimetrically. [d] Number-average molecular weight ($\bar{M}_n$) and polydispersity index ($\bar{M}_w/\bar{M}_n$) obtained by using gel permeation chromatography (GPC) with linear poly(styrene) standards in tetrahydrofuran at 40 °C.

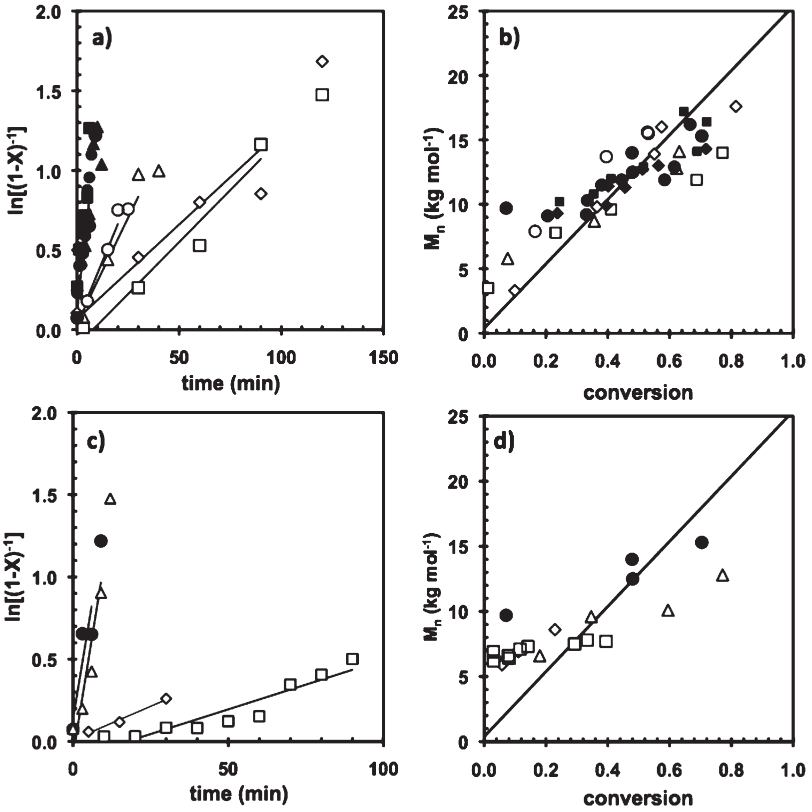

Figure 1. (a) Plot of $\ln[(1 - X)^{-1}]$ (X = monomer conversion) versus time and (b) plot of number-average molecular weight ($\bar{M}_n$) versus X for styrene/maleic anhydride (S/MA) copolymerizations in 50 wt % dioxane at 110 °C for various MA initial molar feed compositions $f_{MA,0} = 0.10$ (SMA-1, □), $f_{MA,0} = 0.20$ (SMA-2, ◇), $f_{MA,0} = 0.30$ (SMA-3, △), $f_{MA,0} = 0.40$ (SMA-4, ○), $f_{MA,0} = 0.45$ (SMA-4.5, ▲), $f_{MA,0} = 0.49$ (SMA-5, ●), and $f_{MA,0} = 0.55$ (SMA-5.5, ■). (c) Plot of $\ln[(1 - X)^{-1}]$ versus time and (d) plot of M_n versus X for S/MA copolymerizations in 50 wt % dioxane at various temperatures for fixed MA initial molar feed compositions $f_{MA,0} \approx 0.50$ and r = [SG1]$_0$/[BlocBuilder]$_0$ = 0.05: at 80 °C (SMA-7, □), at 90 °C (SMA-6, ◇), at 100 °C (SMA-8, △), and at 110 °C (SMA-5, ●). The copolymerizations noted by SMA-1 to SMA-8 are listed in Table 1.

measured using gel permeation chromatography (GPC, Water Breeze) with tetrahydrofuran (THF) as the mobile phase. A mobile phase flow rate of 0.3 mL min^{-1} was applied, and the GPC was equipped with three Waters Styragel HR columns (HR1 with molecular weight measurement range of 10^2−5×10^3 g mol^{-1} (particle size of 3 μm), HR2 with molecular weight measurement range of 5×10^2−2×10^4 g mol^{-1} (particle size of 3 μm), and HR4 with molecular weight measurement range 5×10^3−6×10^5 g mol^{-1} (particle size of 3 μm)) and a guard column was used. The columns were heated to 40 °C during the analysis. The molecular weights were determined by calibration with linear narrow molecular weight distribution poly(styrene) standards, and the GPC was equipped with both ultraviolet (UV 2487) and differential refractive index (RI 2410) detectors. The UV detector was set to a wavelength of 255 nm to detect the aromatic rings in the poly(styrene) containing copolymers.

^{13}C NMR (resonance frequency of 75 MHz) was performed in a 300 MHz Varian Mercury spectrometer under similar conditions to those previously reported by Ha.[22] The copolymer samples were dissolved in *d*-acetone using 5 mm diameter Up NMR tubes, and the ^{13}C NMR characterizations were performed using a flip angle of 30°, a relaxation time of 5 s, and suppression of the NOE.

Results and Discussion

Nitroxide-Mediated Polymerization Kinetics. Figure 1a indicates the scaled conversion ($\ln(1 - X)^{-1}$ versus time where X = monomer conversion) for experiments done at identical temperatures (110 °C) and ratios of free nitroxide to BlocBuilder unimolecular initiator (r = [SG1]$_0$/[BlocBuilder]$_0$ = 0.05) while varying the initial molar feed concentration of maleic anhydride ($f_{MA,0}$). Figure 1b indicates the number-average molecular weight $\bar{M}_n$ versus X for the same set of experiments shown in Figure 1a. Figure 1c shows $\ln(1 - X)^{-1}$ versus time for polymerizations done at various temperatures ranging from 80 to 110 °C at a fixed r = 0.05 and initial monomer feed of approximately $f_{MA,0}$ = 0.5. Figure 1d shows the $\bar{M}_n$ versus X corresponding to the experiments shown in Figure 1c. The slopes from Figure 1a,c were used to estimate the apparent rate constant $k_p[P^\bullet]$ where k_p is the propagation rate constant and $[P^\bullet]$ is the concentration of propagating macroradicals. Table 1 summarizes the experimental conditions and the kinetic data in terms of the product of the propagation rate constant k_p and the equilibrium constant K between the dormant and active chains. Such a parameter is frequently cited in nitroxide-mediated controlled radical polymerization since it combines two of the relevant controlling factors for the pseudo-"living" nature of the polymerization.[23,24] K is defined as follows:

$$K = \frac{[P^\bullet][N^\bullet]}{[P{-}N]} \tag{1}$$

where $[P^\bullet]$ is the concentration of propagating macroradicals, $[N^\bullet]$ is the concentration of free nitroxide, and [P−N] is the concentration of the dormant alkoxyamine-terminated chains. The parameter k_pK can be obtained from the slope of the semilogarithmic kinetic plots ($k_p[P^\bullet]$) and some assumptions regarding K. First, during the initial stages of the polymerization, the initial concentration of the nitroxide $[N^\bullet]_0$ is sufficiently high so that its concentration does not dramatically change and is effectively constant ($[N^\bullet] \approx [N^\bullet]_0$). Additionally, during the initial stages of the polymerization where there is not excessive termination of alkoxyamine-terminated species, the concentration of alkoxyamine dormant species should be nearly identical to the initial initiator concentration ($[\mathrm{P{-}N}] \approx [\mathrm{BlocBuilder}]_0$. Thus, k_pK can be estimated using the kinetic data and the initial molar ratio of free nitroxide to BlocBuilder initiator ($r = [\mathrm{SG1}]_0/[\mathrm{BlocBuilder}]_0$) provided the kinetic data are taken in the range (i.e., low conversion) where the noted assumptions are likely to be met (eq 2).

$$k_pK \cong k_p\frac{[\mathrm{P}^\bullet][\mathrm{SG1}]_0}{[\mathrm{BlocBuilder}]_0} = k_p[\mathrm{P}^\bullet]r \qquad (2)$$

The experimental k_pK's are summarized in Table 2 for the various experiments. Note that in the case of a copolymerization between two monomers an average k_p or K must be used to describe the kinetics. Average k_p's have been derived previously for copolymerizations assuming terminal and penultimate unit effect models.[25] In the case of a system such as styrene/maleic anhydride where alternating structures are expected, a penultimate model would better describe the propagation kinetics. Sanayei et al. defined the mean k_p, $\langle k_p\rangle$, for S/MA copolymerizations given that MA does not homopolymerize (taking S to be monomer "1" and MA to be monomer "2") as follows.[26] Thus, $k_{122} = k_{222} = 0$ and then $\bar{r}_2/\bar{k}_{22} = 1/k_{121}$ in this case, giving eq 3.

$$\langle k_p\rangle = \frac{\bar{r}_1 f_1^{\,2} + 2f_1f_2}{\dfrac{\bar{r}_1 f_1}{\bar{k}_{11}} + \dfrac{f_2}{k_{121}}} \qquad (3)$$

$$\bar{r}_1 = \frac{r_{21}(f_1r_{11} + f_2)}{f_1r_{21} + f_2}, \quad \bar{k}_{11} = \frac{k_{111}(r_{11}f_1 + f_2)}{r_{11}f_1 + \dfrac{f_2}{s_1}}, \quad s_1 = \frac{k_{211}}{k_{111}}$$

The f_i's are the mole fractions of monomer "i" in the feed while the r_{ij}'s ($r_{11} = k_{111}/k_{112}$, $r_{21} = k_{211}/k_{212}$) are the monomer reactivity ratios and the relevant radical reactivity ratio is s_1 as defined above. The mean equilibrium constant $\langle K\rangle$ between the dormant SG1-capped chain ([P−N]) and the free SG1 ($[\mathrm{N}^\bullet]$ and active radical chain end ($[\mathrm{P}^\bullet]$) for a binary copolymerization was derived by Charleux and co-workers for both terminal and implicit penultimate unit effect (IPUE) models in terms of the f_i's and equilibrium constants K_i for the individual homopolymerizations.[21] Care should be noted in the definitions of K as often K's from the homopolymerizations are applied in the determination of $\langle K\rangle$. Although MA does not homopolymerize, the chain ends can be capped with MA units so K's should be defined as those of the monomer unit attached to the nitroxide. We did not have K_{MA} (defined herein as the equilibrium between chain ends terminated with MA and the SG1 capping species) experimentally available to us so we used K_{S} (defined herein as the equilibrium constant between chain ends terminated with styrene and the SG1 capping species) as a comparison to our data. Thus, our copolymerization kinetic data from NMP was compared to that predicted from $\langle k_p\rangle$ for S/MA conventional radical copolymerization and K_{S} from styrene homopolymerizations provided in the literature at the appropriate temperature. All k_p parameters for the IPUE were obtained from pulsed laser polymerization measurements by Sanayei et al. with the exception of the homopolymerization propagation rate constant for styrene, k_{111}, which was taken from Buback et al. ($k_{111} = 10^{7.630}$ L mol^{-1} s^{-1} exp[(−32.51 kJ mol^{-1})/RT][27]). K_{S} for styrene was estimated from literature ESR experiments[17] and our own estimates from k_pK measurements at various temperatures together with literature k_{111} values.[28] K_{S} for styrene at 110 °C was estimated to be 1.7×10^{-9} mol L^{-1} at 110 °C and was used in all calculations here.

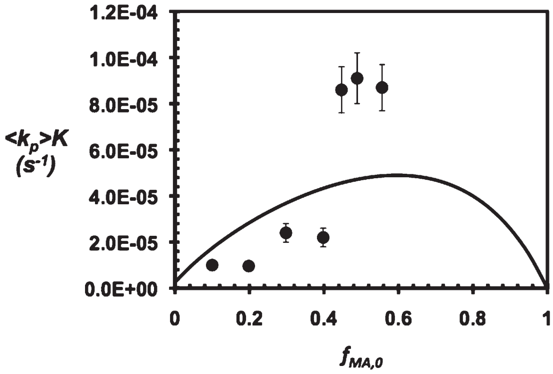

Figure 2. Product of the average propagation rate constant, $\langle k_p\rangle$, with the average equilibrium constant, $\langle K\rangle$, $\langle k_p\rangle\langle K\rangle$, for maleic anhydride/styrene copolymerizations at 110 °C in 1,4-dioxane versus initial molar feed composition of styrene ($f_{\mathrm{styrene},0}$). The experimental data are indicated by the filled circles (●) with error bars associated with each data point derived from the standard error of the slope from the semilogarithmic kinetic plots, while the theoretical $\langle k_p\rangle\langle K\rangle$ values were determined using the combination of the $\langle k_p\rangle$ from eq 3 and the K for NMP of styrene at 110 °C (solid line).

Comparison of experimentally estimated k_pK's as a function of initial MA feed concentration for NMP of S/MA copolymerization at 110 °C against that predicted using the assumptions above and literature data is shown in Figure 2. Increasing MA feed content dramatically increased the polymerization rate, particularly sharply when $f_{\mathrm{MA},0} > 0.4$. Polymerizations with $f_{\mathrm{MA},0} \sim 0.5$ were very rapid at 110 °C, typically becoming extremely viscous after only a few minutes of polymerization with X approaching 0.6 and k_pK nearly 1×10^{-5} s^{-1}. By contrast, a styrene homopolymerization at the same temperature had a k_pK about an order of magnitude lower with $k_pK \approx 2 \times 10^{-6}$ s^{-1}.[28] The acceleration in the polymerization rate with increasing MA feed concentration was also noted in RAFT copolymerization studies by Chernikova et al.[13] At 60 °C using *S*-benzyldithiobenzoate as the RAFT chain transfer agent, they reported that the initial conversion rate increased ~5-fold as the $f_{\mathrm{MA},0}$ increased from 0.1 to 0.5.

Note that the predicted fit did not match our experimental data too closely. Obviously, our assumption for the equilibrium constants does not hold very well. Better estimates for K of the S/MA copolymerizations mediated by BlocBuilder could potentially be ascertained from electron spin resonance (ESR) studies. Future experiments could copolymerize styrene/MA mixtures with excess MA in the feed so that chain ends will be capped with MA units. Also, such copolymerizations should be taken to fairly low conversion so that the SG1 termini are retained. (^{31}P would be useful to determine the fraction of SG1 units on the chain end.) ESR in combination with a radical scavenger could then be performed on the SG1-terminated copolymer to determine the concentration of SG1 released that can be related back to the equilibrium constant.

If the polymerizations were pseudo-"living", a plot of $\bar{M}_n$ versus X would be linear. In Figure 1b, such plots are shown for various $f_{\mathrm{MA},0}$ at 110 °C in 50 wt % dioxane solutions along with the theoretical $\bar{M}_n$ versus X (shown by the solid line). At low conversions, some $\bar{M}_n$'s are above the theoretical line as the precipitation process used to recover the polymer may have preferentially precipitated the polymers with higher molecular weight. At $X > 0.5$, solutions became extremely viscous and the $\overline{M}_n$ tended to level with conversion, likely due to irreversible termination reactions. Generally as the $f_{MA,0}$ increased, the molecular weight distributions broadened slightly, with $\overline{M}_w/\overline{M}_n$ increased to nearly 1.3 at $f_{MA,0} = 0.49$ (Table 2). Increasing the concentration of free nitroxide from $r = 0.05$ to 0.10 at a polymerization temperature of 110 °C and $f_{MA,0} = 0.49$ (entry SMA-9 in Tables 1 and 2) did not significantly decrease the polymerization rate although when the monomer concentration was diluted from 50 to 25 wt %, the k_pK did decrease (entry SMA-10 in Tables 1 and 2). In both of these latter cases, the $\overline{M}_w/\overline{M}_n$'s did not significantly decrease as expected if the polymerization was more controlled.

Nitroxide-mediated polymerizations using BlocBuilder are often characterized by the possibility of such polymerizations being run at temperatures as low as 90 °C, ~30 °C lower than typically done with first generation nitroxide mediators such as TEMPO. Considering that the S/MA copolymerizations studied here polymerized so rapidly at 110 °C when the feed composition was nearly equimolar, it was useful to determine whether the copolymerization could be done at a lower temperature and be more controlled compared to the cases examined above. For equimolar feed compositions, the effect of temperature on the polymerization rate is expressed by the $\ln[(1 - X)^{-1}]$ versus time plots in Figure 1c. The $\langle k_p \rangle K$ values derived from the slopes of such plots are summarized in Table 1 and are reduced by a factor of nearly 20 upon changing the temperature from 110 to 80 °C. Although the polymerization rate was decreased significantly by temperature, the control of the polymerization was not necessarily duplicated. As seen in Figure 1d, the $\overline{M}_n$ versus X plots tended to be quite linear up to $X \approx 0.5$. Again, as in the case of the copolymerizations done at 110 °C shown in Figure 1a, at low polymerizations some fractionation is likely as the recovered polymer $\overline{M}_n$'s were above that of the theoretical line. However, expected improvements in controlling the molecular weight distribution by lowering the polymerization temperature were not realized. The $\overline{M}_w/\overline{M}_n$'s actually increased as the temperature was decreased with $\overline{M}_w/\overline{M}_n = 1.3-1.4$ at the lowest temperatures (Table 2). The increased broadening is due likely to the decomposition of the BlocBuilder perhaps not being fast enough to provide sufficient control.

Chain Extension with Styrene from a Poly(styrene-*alt*-maleic anhydride) Macroinitiator. A macroinitiator (entry SMA-5 in Table 2, $\overline{M}_n = 15.5$ kg mol^{-1}, $\overline{M}_w/\overline{M}_n = 1.31$, $F_{MA} = 0.48$), with what was later found to possess a nearly strictly alternating microstructure (see the Copolymer Composition section) was used to reinitiate a fresh batch of styrene. The molecular weight increased, suggesting chain extension, but the molecular weight distribution of the chain-extended species was rather broad and suggests that the macroinitiator possessed a substantial concentration of dead chains. The chain extended copolymer had $\overline{M}_n = 35.3$ kg mol^{-1}, $\overline{M}_w/\overline{M}_n = 1.60$, and $F_{MA} = 0.05$ (Figure 3). This is not surprising as the macroinitiator was formed from a copolymerization that went to relatively high conversion ($X = 0.70$) and likely had a high concentration of irreversibly terminated chains. Still, this particular chain-extension experiment was useful as the ^{13}C NMR could be used to clearly discern between strictly alternating S/MA sequences and homogeneous triads of styrene (see the Copolymer Composition section). The increase in styrene composition from $F_s = 0.52$ in the macroinitiator to $F_s = 0.95$ in the final copolymer roughly coincides with the obtained GPC results although the fraction of styrene seems higher in the final block copolymer. Perhaps some fractionation of the copolymers was occurring during the polymer recovery where chains with more MA were not being precipitated as easily.

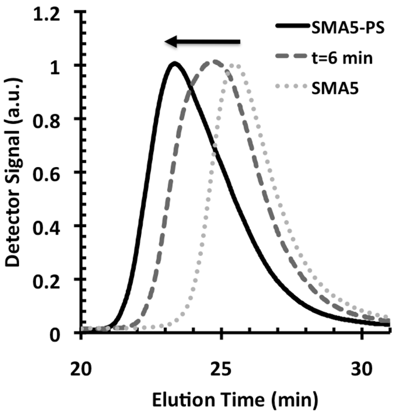

Figure 3. Gel permeation chromatograms for styrene chain extensions from an alternating styrene/maleic anhydride macroinitiator (SMA5 in Table 2, with $\overline{M}_n = 15.5$ kg mol^{-1}, $\overline{M}_w/\overline{M}_n = 1.31$, and $F_s = 0.52$); an intermediate sample after a polymerization time of $t = 6$ min ($\overline{M}_n = 25.0$ kg mol^{-1}, $\overline{M}_w/\overline{M}_n = 1.50$), and the final sample taken after $t = 72$ min (SMA5-PS, with $\overline{M}_n = 35.3$ kg mol^{-1}, $\overline{M}_w/\overline{M}_n = 1.60$, and $F_s = 0.95$. The chain extension was done in 50 wt % 1,4-dioxane solution at 115 °C.

Copolymer Composition. As reported by Ha,[22] triad sequences of styrene (S) and maleic anhydride (M) in a copolymer could be determined by ^{13}C NMR. Using this technique, we can determine whether the copolymer microstructure is alternating (SMS), semialternating (SSM or MSS), or nonalternating (SSS). There are two predominant markers; the first is the resonance representing the aromatic carbon closest to the backbone belonging to the styrene (labeled as C7 in Figure 4), and the second is the resonance of the CH$_2$ group on the aliphatic backbone belonging to styrene (labeled as C1 in Figure 4). A perfectly alternating sequence (SMS) will have a C7 resonance at $\delta = 137-140$ ppm and a C1 resonance at $\delta = 33-37$ ppm. A polymer which has more styrene (sequences such as SSM to SSS) will experience an upfield shift of these resonances to $\delta = 145-148$ ppm for C7 and $\delta = 42-47$ ppm for C1.[22] As previously mentioned, copolymer samples SMA7 through SMA10 (Table 1) were polymerized at temperatures ranging from 80 to 110 °C using nearly equimolar initial feed mixtures of the monomers. In all cases, the C7 and C1 peaks are indicative of alternating SMS sequences with no evidence of significant concentrations of SSM or SSS sequences. Characteristic spectra for SMA7 (polymerized at 80 °C) and SMA10 (polymerized at 110 °C) are shown in Figure 4, and both do not show the shift expected at $\delta = 145-148$ ppm if SSM or SSS triads were present. Similar results were obtained for equimolar feeds using RAFT done at 60 °C[13] but never by NMP at such high temperatures. Thus, polymerization of nearly equimolar S/MA feeds at temperatures of 80−110 °C using NMP with BlocBuilder resulted in copolymers with nearly completely alternating microstructures. However, whether strictly alternating microstructures occur at different feed compositions at such high polymerization temperatures still needed to be confirmed.

Experiments SMA1 through SMA4 had $f_{MA,0} < 0.40$ and were all performed at 110 °C (Table 1). As expected, the final copolymer compositions as determined by ^{13}C NMR were richer in styrene (Table 2). When examining the C7 and C1 resonances, there was an apparent upfield shift relative to the

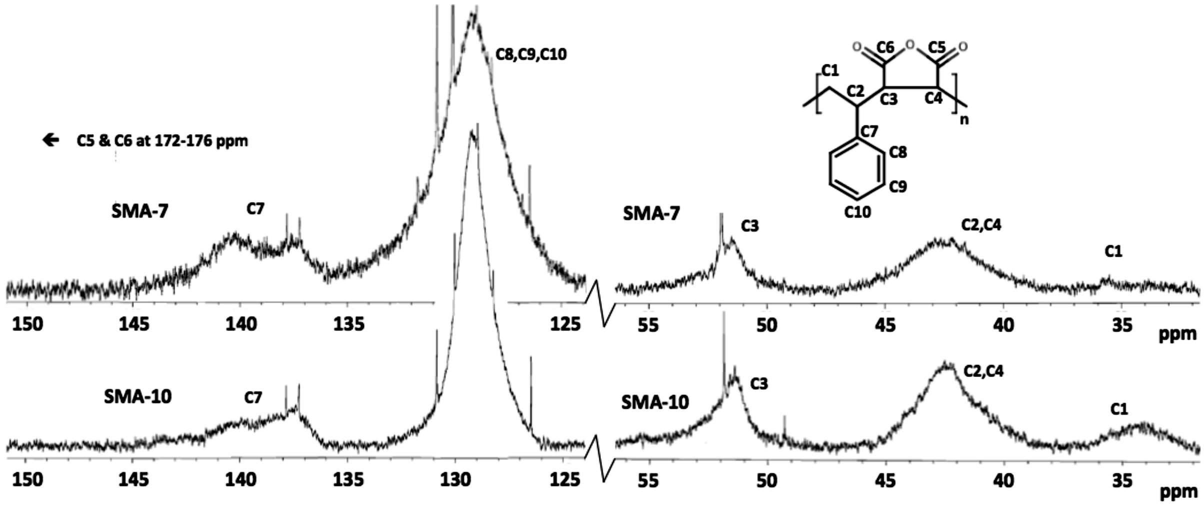

Figure 4. ^{13}C NMR spectra of styrene/maleic anhydride copolymers with assignments of carbon resonances for SMA-7 (polymerized at 80 °C) and SMA-10 (polymerized at 110 °C) using BlocBuilder. All characteristics for SMA-7 and SMA-10 are summarized in Tables 1 and 2.

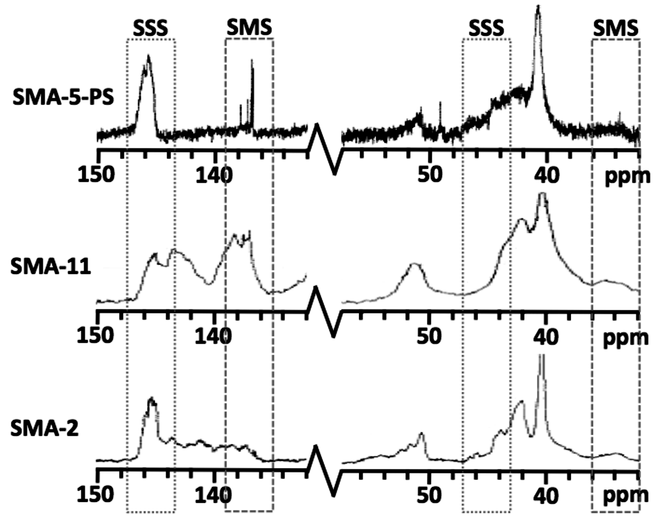

Figure 5. ^{13}C NMR spectra of styrene/maleic anhydride copolymers with assignments of carbon resonances for SMA-5-PS (where $f_{\mathrm{S,0}} \approx f_{\mathrm{MA,0}}$ for copolymerization followed by chain extension with styrene to give P(S-*alt*-MA)-*b*-PS); SMA-11 ($f_{\mathrm{MA,0}}$ = 0.2) copolymerization done at 90 °C to give P(S-*alt*-MA)-*b*-PS) and SMA-2 ($f_{\mathrm{MA,0}}$ = 0.2) copolymerization done at 110 °C to give P(S-*ran*-MA)) using BlocBuilder. The dotted line represents the pure styrene segments (SSS, δ = 145−148 ppm and δ = 42−47 ppm) whereas the dashed line represents the alternating sequences (SMS, δ = 136−141 ppm and δ = 32−37 ppm) and between these two areas represents the semialternating sequences (SSM and MSS, δ = 142−145 ppm and δ = 37−42 ppm). All characteristics for SMA5-PS, SMA-11, and SMA-2 are summarized in Tables 1 and 2.

decrease in $f_{\mathrm{MA,0}}$. With a decrease in $f_{\mathrm{MA,0}}$, the appearance of MSS and SSM triads became evident, and with further decreases in $f_{\mathrm{MA,0}}$, a higher proportion of SSS triads were observed. For example, SMA1, which had $f_{\mathrm{MA,0}} = 0.10$ and a final copolymer composition $F_{\mathrm{MA}} = 0.15$, had a C7 resonance at δ = 145−147 ppm and a C1 resonance at δ = 42−44 ppm. There was no clear evidence of any resonances attributed to alternating microstructures, although this may have been expected with such high styrene feed content and elevated polymerization temperatures.[14]

Note that the copolymer compositions for SMA-1 through SMA-4 were not dramatically different compared to the initial feed compositions which suggests alternating copolymerizations were not occurring at the higher polymerization temperatures. The ^{13}C NMR spectrum of sample SMA5 ($f_{\mathrm{MA,0}} = 0.49$) was similar to the spectra obtained from SMA7 and SMA10: almost exclusively alternating sequences were present with F_{MA} = 0.49. To conclusively determine whether indeed the copolymers consisted of initially alternating sequences followed by styrene homopolymerization once all MA in the feed was exhausted, two tests were performed. In the first test, SMA5 (an alternating S/MA copolymer) was used as a macroinitiator to initiate a fresh batch of styrene (sample SMA5-PS, see Table 2). The second test involved polymerizing a styrene-rich feed ($f_{\mathrm{MA,0}} = 0.2$) at a much lower polymerization temperature of 90 °C.

As seen in Figure 5 for the styrene chain extension from the alternating S/MA macroinitiator SMA-5, the ^{13}C NMR spectrum indicated two resonances were present for C7: one resonance at 137−141 ppm corresponding to SSS triads and another at 145−147 ppm corresponding to alternating SMS triads. As mentioned, SMA5-PS, regardless of the relatively high $\overline{M}_{\mathrm{w}}/\overline{M}_{\mathrm{n}}$, consists of one block of strictly alternating SMS sequences and another block consisting strictly of styrene. These distinct sets of resonances corresponding to the diblock where one block was alternating and the other was homopoly(styrene) were not observed for samples SMA-1 through SMA-4. Instead, intermediate peaks corresponding to SSM or MSS triads were observed (SMA-2 as an example, Figure 5). This demonstrates that polymerizations done at 110 °C using styrene-rich molar feed ratios ($f_{\mathrm{MA,0}} < 0.5$) will result in random S/MA copolymers with no alternating sequences. A nearly equimolar feed polymerized at 110 °C will however result in a copolymer with nearly a completely alternating microstructure. The formation of the poly(S-*alt*-MA)−poly(styrene) block from the alternating copolymer macroinitiator shows such a block copolymer can be obtained at higher polymerization temperatures in a two-step process. However, can such a block copolymer be obtained in a single step process by NMP as desired by other researchers earlier? Polymerization of a styrene-rich feed at a lower temperature was thus tested.

The experiment SMA-11 had a styrene rich feed of $f_{\mathrm{MA,0}}$ = 0.2 and was performed at 90 °C. Again, ^{13}C NMR was used to determine the type of triads present in the copolymer. The ^{13}C NMR of SMA-11 shown in Figure 5 possesses many similarities to that of SMA-5-PS. The two major triads for SMA-11 are those pertaining to SMS (composition of SMS triad in final copolymer estimated by ^{13}C NMR = $F_{SMS} = 0.57$) and SSS ($F_{SSS} = 0.27$) with a much lower proportion of SSM/MSS triads ($F_{SSS} = 0.16$). This is strong evidence that NMP using BlocBuilder initiator at 90 °C can provide a one-step block copolymer consisting of a largely alternating S/MA segment and another segment consisting of homopoly(styrene). Thus, NMP can join RAFT as a possible controlled radical polymerization method to produce nearly strictly alternating S/MA sequences in block copolymers.

Conclusions

Styrene/maleic anhydride (S/MA) copolymerizations at initial molar MA feed concentrations from $f_{MA,0} = 0.10-0.55$ were performed at temperatures from 80 to 110 °C using BlocBuilder unimolecular initiator in 1,4-dioxane solution. This study examined the copolymerization kinetics and the resulting copolymer microstructures. As $f_{MA,0}$ increased, the apparent rate constants increased dramatically with copolymerizations performed at nearly equimolar feeds $f_{MA,0} = 0.45-0.55$ having k_pK (k_p = propagation rate constant, K = equilibrium constant between active and dormant nitroxide-terminated chains) values about 20 times higher compared to styrene homopolymerization using the same BlocBuilder initiator at 110 °C. Similar trends in acceleration were observed in both conventional radical S/MA copolymerization and RAFT copolymerizations.

S/MA copolymerizations performed at 110 °C did not possess a high concentration of SMS alternating structures when $f_{MA,0} = 0.1-0.4$ as indicated by ^{13}C NMR. However, at nearly equimolar feeds at 110 °C, nearly alternating SMS structures were observed, suggesting that the alternating sequences were "forced" by the feed conditions. Subsequent chain extension from an alternating S/MA copolymer macroinitiator with a second batch of styrene indicated that the macroinitiator was sufficiently "living" as indicated by a shift in the GPC chromatograms to higher molecular weights although the product was relatively broad. It should be noted that the macroinitiator was not necessarily ideal as it was synthesized to relatively high conversion ($X = 0.7$), and the concentration of dead macroinitiator chains due to irreversible termination reactions may have been higher than desirable. ^{13}C NMR of the chain-extended species showed the presence of two triads: one segment consisting of an alternating S/MA microstructure and the other consisting of a homopoly(styrene) segment. Thus, under appropriate conditions (i.e., equimolar feed conditions), a diblock where one block consists of alternating S/MA sequences and the other block consists of poly(styrene) can be done in a two-step process at temperatures of 110−115 °C.

A S/MA nitroxide-mediated copolymerization done at 90 °C with a styrene-rich feed composition ($f_{MA,0} = 0.2$) was done to determine whether the poly(S-*alt*-MA)-*b*-poly(S) diblock could be done in a single step. ^{13}C NMR revealed two significant populations of triads. One triad corresponded to SMS alternating sequences, and the other corresponded to SSS homopoly(styrene) sequences. Triads corresponding to SSM or MSS sequences were much lower by comparison. The ability of BlocBuilder to control NMP at lower temperatures of 90 °C has thus enabled the use of NMP to provide one-step block copolymers consisting of a block of nearly alternating S/MA sequences and the other of pure poly(styrene). These results open an additional path toward the use of controlled radical polymerization processes to produce novel microstructured maleic anhydride containing copolymers of use to many technologies.

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