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ARTICLE

Poly(*tert*-butyl methacrylate/styrene) Macroinitiators as Precursors for Organo- and Water-Soluble Functional Copolymers Using Nitroxide-Mediated Controlled Radical Polymerization

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ABSTRACT: Styrene/*tert*-butyl methacrylate (S/TBMA) mixtures, with initial TBMA molar feed compositions $f_{\mathrm{TBMA},0} = 0.1-0.92$, were copolymerized by nitroxide-mediated polymerization (NMP) in bulk at 90 °C using 10 mol % {*tert*-butyl[1-(diethoxyphosphoryl)-2,2-dimethylpropyl]amino} nitroxide (SG1) relative to 2-({*tert*-butyl[1-(diethoxyphosphoryl)-2,2-dimethylpropyl]amino}oxy)-2-methylpropionic acid unimolecular initiator (BlocBuilder) to form SG1-terminated macroinitiators. k_pK values (k_p = propagation rate constant, K = equilibrium constant) for S/TBMA increased significantly as $f_{\mathrm{TBMA},0}$ increased, with $k_pK = (7.4 \pm 0.03) \times 10^{-7}$ to $(5.4 \pm 0.9) \times 10^{-5}$ s^{-1}. Copolymer reactivity ratios were $r_{\mathrm{TBMA}} = 0.13-0.27$ and $r_S = 0.43-0.59$ using Fineman–Ross, Kelen–Tüdos, and nonlinear least-squares fitting to the Mayo–Lewis terminal model. All S/TBMA copolymers (number-average molecular weight $\bar{M}_n = 4.5-15.6$ kg mol^{-1}) exhibited low polydispersities ($\bar{M}_w/\bar{M}_n \leq 1.30$), and $\bar{M}_n$ exhibited linear behavior with conversion up to 25–40% and monomodal molecular weight distributions. TBMA-rich copolymer ($\bar{M}_n$ = 14.2 kg mol^{-1} and $\bar{M}_w/\bar{M}_n = 1.30$) was shown to have a high degree of "livingness" based upon ^{31}P NMR measurements for the SG1 end group (≈75%), and successful reinitiations of fresh batches of styrene, *tert*-butylstyrene, *N*-isopropylacrylamide, and a ternary mixture of glycidyl methacrylate/methyl methacrylate/styrene (all products were monomodal with $\bar{M}_n$ = 17.8–81.0 kg mol^{-1} and $\bar{M}_w/\bar{M}_n = 1.33-1.59$).

Introduction

Since its discovery in the early 1990s, controlled radical polymerization (CRP) has received considerable attention due to its ability to produce a variety of functional and highly defined materials that traditionally would only be attainable by ionic or other "living" polymerization techniques.[1] Now, CRP techniques allow access to such well-defined polymers like block copolymers, which have long been studied due to their self-assembly into ordered microstructures.[2] CRP techniques have been targeted to produce block copolymers for next-generation biomaterials,[3-7] organic electronics,[8-10] and nanoporous materials.[11-13] For the latter application, amphiphilic block copolymers with polar segments are of particular interest for next-generation separation media.[12] Such amphiphilic block copolymers are also desirable as surfactant-free emulsion polymerization initiators.[14,15]

Amphiphilic block copolymers typically require incorporation of a polar monomer into the polymer chains, for example, one with an acidic functional group such as acrylic acid. CRP of acrylic acid is attractive since functional group protection is not generally required, unlike the case with "living" ionic polymerization.[1] Consequently, poly(acrylic acid) controlled microstructures have been accessed by the main CRP methods such as reversible addition–fragmentation transfer (RAFT),[16-18] nitroxide-mediated polymerization (NMP), and atom transfer radical polymerization (ATRP) although in the case of ATRP, poisoning of the metal–ligand catalyst by acrylic acid was an issue.[19] NMP methods to produce poly(acrylic acid) have particularly been facilitated by the advent of acyclic nitroxides such as SG1 ({*tert*-butyl [1-(diethoxyphosphoryl)-2,2-dimethylpropyl]amino} nitroxide) or TIPNO (2,2,5-trimethyl-4-phenyl-3-azahexane nitroxide) which have enabled controlled polymerization of acrylates and have permitted polymerizations to occur at temperatures as low as 90 °C, which was not generally possible with earlier nitroxides such as 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO). Unimolecular initiators based on SG1 such as 2-methyl-2-[*N*-*tert*-butyl-*N*-(diethoxyphosphoryl-2,2-(dimethylpropyl)aminooxy]propionic acid (BlocBuilder, Arkema; see Scheme 1 for structures of the initiators/mediators) have expanded the utility of NMP by enabling miniemulsion polymerization at temperatures lower than 100 °C and a carboxylic functionality that allows solubility in water when neutralized.[20-23] Despite these advantages, several drawbacks toward polymerizing acrylic acid using alkoxyamines such as SG1 and BlocBuilder are the possibilities of degradation reactions by the organic acid with the alkoxyamine[24-26] and the loss of propagating radical due to β-hydrogen transfer to SG1.[27,28] The consequent loss of the SG1-terminated chains leads to poor control over the polymerization and failure to cleanly extend the chains with a second batch of monomer to make block copolymer. Thus, it may be ultimately better to use a protected form of acrylic acid such as *tert*-butyl acrylate when employing NMP and then later remove the *tert*-butyl protecting group. Such a route has proven to be effective toward accessing poly(acrylic acid)-containing block copolymers.[25]

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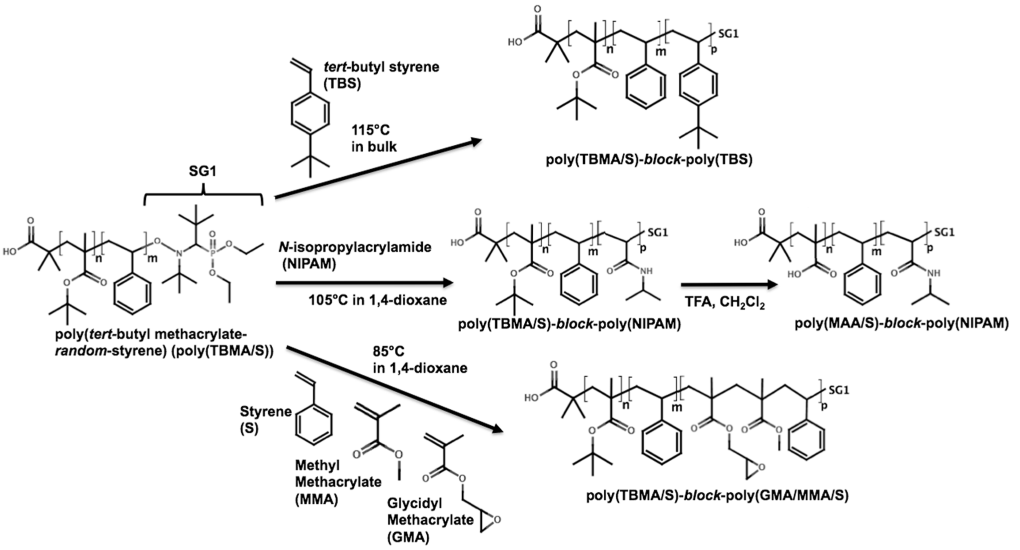
Scheme 1. Schematic of Chain Extensions with Various Functional Monomers from *tert*-Butyl Methacrylate (TBMA)-Rich Macroinitiator Done in Bulk or in Solvent at Different Temperatures



Compared to acrylates, methacrylates experience significantly lower probabilities of intramolecular reactions (backbiting) or other chain transfer reactions during polymerization,[29,30] and thus the use of methacrylic acid may be preferable to avoid such side reactions that could potentially alter the desired microstructure. To avoid the degradative reaction of the acid with the alkoxyamine, the use of *tert*-butyl methacrylate (TBMA) is desirable. Although the controlled polymerization of TBMA has been accomplished by other CRP methods like atom transfer radical polymerization (ATRP),[31,32] NMP with TBMA has not been described thoroughly, likely due to the relatively high equilibrium constant K between active and dormant chains exhibited by methacrylates[33] which leads to a higher probability of irreversible termination reactions. The controlled polymerization of methacrylates by NMP has been relatively elusive although enormous strides have been made recently toward polymerizing feeds of pure methacrylic monomers or with a small amount of comonomer (~10% of the comonomer). Detrembleur et al. homopolymerized TBMA in water using nitroxide precursors formed *in situ* from sodium nitrite,[34,35] nitroso compounds, and nitric oxides.[36] At 80 °C in water when using a $NaNO_2/FeSO_4/K_2S_2O_8$ initiator/mediator system, the heterogeneous polymerization of TBMA resulted in a linear relationship between the number-average molecular weight ($\bar{M}_n$) versus TBMA conversion up to conversions ~50% and $\bar{M}_n$ approaching 60 kg mol^{-1} with polydispersity indexes $\bar{M}_w/\bar{M}_n$ being maintained ~1.2. Chain extensions from the poly(TBMA) were not described although the general procedure was later described for a wide number of acrylic and styrenic block copolymers.[37] Later, Guillaneuf et al. showed that bulk polymerization of methyl methacrylate (MMA) without any comonomer was also possible using DPAIO (2,2-diphenyl-3-phenylimino-2,3-dihydroindol-1-yloxyl nitroxide) as the controller. The bulk MMA polymerization indicated that $\bar{M}_n$ increased with conversion up to 60% with $\bar{M}_n = 17$ kg mol^{-1} and $\bar{M}_w/\bar{M}_n = 1.35$ after 8 h at 100 °C. Chain extension of the PMMA−DPAIO with *n*-butyl acrylate at 120 °C was inhibited relatively quickly due to the extremely low decomposition rate constant k_d for the poly(*n*-butyl acrylate)−DPAIO segment.

Polymerization of various methacrylates such as methacrylic acid, MMA,[38,39] poly(ethylene glycol) methacrylate (PEGMA),[40] ethyl methacrylate (EMA),[41] butyl methacrylate (BMA),[41] and glycidyl methacrylate (GMA)/MMA, EMA, and BMA mixtures[41] could be accomplished using BlocBuilder/SG1 at 80−90 °C using a small amount of styrene as a comonomer (4.4−8.8 mol %) to reduce the average equilibrium constant sufficiently to observe linear increases of $\bar{M}_n$ versus conversion and $\bar{M}_w/\bar{M}_n < 1.5$. Such polymerizations have been done in organic media and in miniemulsion conditions, and the resulting methacrylate-rich copolymers exhibited properties that were essentially identical to those of the pure poly(methacrylates).[42,43] Under appropriate conditions, chain extensions with other methacrylates were accomplished, indicating a high degree of "livingness" of the macroinitiators.[42] Thus, a route to obtain poly(TBMA) and associated block copolymers by NMP with BlocBuilder/SG1 should be possible.

The following study endeavors first to find how NMP can produce TBMA-containing copolymers that would be suitable for subsequent chain extensions with other monomers. Initially, the effect of feed composition on the kinetics and the composition of TBMA/styrene (TBMA/S) random copolymers with BlocBuilder/SG1 will be studied. This is essential toward designing block or gradient copolymers with acidic groups, which become accessible after removal of the *tert*-butyl protecting groups. Subsequent chain extensions with various monomers will reflect the utility of using poly(TBMA/S) precursors to make amphiphilic block copolymers with organo-soluble segments possessing comparably higher glass transition temperatures (via the use of *tert*-butylstyrene), potentially cross-linkable segments (via the use of the epoxy functional GMA), and water-soluble thermosensitive block copolymers (via the inclusion of *N*-isopropylacrylamide in the second block and suitable removal of *tert*-butyl protecting groups from the poly(TBMA/S) segment).

Experimental Section

Materials. Styrene (99%), *tert*-butyl methacrylate (TBMA, 98%), glycidyl methacrylate (GMA, >97%), methyl methacrylate (MMA, 99%), *N*-isopropylacrylamide (NIPAM, 97%), basic alumina (Brockmann, Type 1, 150 mesh), and calcium hydride (90−95% reagent grade) were obtained from Aldrich while methanol (99.8%) was received from Fisher. TBMA, GMA, MMA, and styrene were purified by passage through a column containing a calcium hydride and basic alumina mixture (5 wt % calcium hydride) and were then stored in sealed flasks under a head of nitrogen while NIPAM was recrystallized from hexane. All purified monomers were stored in a refrigerator until required. 2-({*tert*-Butyl[1-(diethoxyphosphoryl)-2,2-dimethylpropyl]amino}oxy)-2-methylpropionic acid, (99%,

Table 1. *tert*-Butyl Methacrylate/Styrene (TBMA/S) Copolymerization Formulations for Various Compositions at 90 °C in Bulk

experiment ID[a]	[BlocBuilder]$_0$ (mol L^{-1})	[SG1]$_0$ (mol L^{-1})	r[b]	[TBMA]$_0$ (mol L^{-1})	[styrene]$_0$ (mol L^{-1})	$f_{\mathrm{TBMA},0}$[c]
TBMA/S-10	0.036	0.003	0.102	0.31	2.06	0.10
TBMA/S-20	0.036	0.003	0.100	0.60	1.76	0.20
TBMA/S-40	0.035	0.003	0.099	1.14	1.20	0.41
TBMA/S-50	0.035	0.003	0.097	1.32	1.02	0.49
TBMA/S-60	0.035	0.003	0.097	1.56	0.76	0.60
TBMA/S-70	0.035	0.003	0.097	1.76	0.55	0.70
TBMA/S-80	0.035	0.003	0.102	1.95	0.36	0.80
TBMA/S-90	0.035	0.003	0.097	2.16	0.14	0.92

[a] Experimental identification ID is given by TBMA/S-*XX*, where TBMA = *tert*-butyl methacrylate and *XX* refers to the initial % molar feed composition of TBMA in the mixture. [b] Initial molar concentration ratio of SG1 free nitroxide to BlocBuilder initiator = r = [SG1]$_0$/[BlocBuilder]$_0$. [c] $f_{\mathrm{TBMA},0}$ is the initial molar feed fraction of *tert*-butyl methacrylate.

BlocBuilder) was purchased from Arkema and was used without further purification. {*tert*-Butyl[1-(diethoxyphosphoryl)-2,2-dimethylpropyl]amino} nitroxide, also known as SG1 (>85%), was kindly donated by Noah Macy of Arkema and used as received. Poly(styrene) (PS, $\bar{M}_n$ = 13.0 kg mol^{-1}, $\bar{M}_w/\bar{M}_n$ = 1.1) and poly(TBMA) ($\bar{M}_n$ = 38.5 kg mol^{-1}, $\bar{M}_w/\bar{M}_n$ = 1.1) used as standards for Fourier transform infrared spectroscopy (FT-IR) were obtained from Scientific Polymer Products Inc.

Synthesis of *tert*-Butyl Methacrylate/Styrene (TBMA/S) Random Copolymers. All TBMA/S random copolymerizations were synthesized in a 100 mL three-neck round-bottom glass flask equipped with a condenser, a thermal well, and a rubber septa. A thermocouple, which was connected to a controller and the heating mantle, was inserted into the thermal well. The reactor contents were mixed using a magnetic stir bar. The initial ratio of monomer and BlocBuilder was calculated to give a copolymer with target number-average molecular weight $\bar{M}_n$ = 25 kg mol^{-1} at complete conversion. All formulations are found in Table 1. For example, for the synthesis of TBMA/S-20, the reactor was sealed, with the rubber septa, after the addition of BlocBuilder (0.533 g, 1.4 mmol), SG1 (0.041 g, 0.14 mmol) ([SG1]/[BlocBuilder] ~ 0.1), and the stir bar. The previously purified monomers, styrene (26.02 g, 250 mmol) and TBMA (8.88 g, 62.5 mmol), were injected with disposable needles into the reactor. An ultrapure nitrogen purge was applied during monomer injection, 30 min postinjection before heating, and over the course of the entire reaction. The mixture was heated to 90 °C at a rate of about 10 °C min^{-1}, and the time at which the reactor reached 90 °C was taken as the start of the reaction (t = 0). Samples were taken by syringe periodically, and the sample polymers were precipitated in a 1:4 distilled water/methanol (w/w) mixture. The resulting polymers were left to settle for several hours and then decanted. The samples were then dried overnight in a vacuum oven at 70 °C to remove any solvent or unreacted monomer. The yield for TBMA/S-20 was 10.4 g (30%) with $\bar{M}_n$=6.7 kg mol^{-1} and $\bar{M}_w/\bar{M}_n$=1.21 relative to poly(styrene) standards by gel permeation chromatography (GPC), and the molar composition of TBMA in the final copolymer was F_{TBMA} = 0.22 using FT-IR spectroscopy (TBMA carbonyl peak at 1720 cm^{-1} and styrene peak at 700 cm^{-1}).

Synthesis of Poly(*tert*-butyl methacrylate-*random*-styrene)-*block*-Poly(styrene) (Poly(TBMA-*r*-S)-*b*-Poly(S)) Block Copolymers. Previously synthesized *tert*-butyl methacrylate/styrene (TBMA/S) copolymers with various TBMA levels were used as macroinitiators to reinitiate a fresh batch of styrene. The formulations for all chain extensions from the random copolymer macroinitiators can be found in Table 2. For example, for the chain extension termed TBMA/S-20-PS in Table 2, previously purified styrene (9.96 g, 95.8 mmol) and the macroinitiator TBMA/S-20 (1.01 g, 0.168 mmol, $\bar{M}_n$ = 6.7 kg mol^{-1}, $\bar{M}_w/\bar{M}_n$=1.21) were mixed with a magnetic stirrer in a 100 mL three-neck round-bottom flask reactor. The reactor setup was identical to that of the one used to synthesize the TBMA/S macroinitiators. The reaction mixture was purged with a steady stream of nitrogen, during styrene addition, for an additional 30 min postinjection and for the entire polymerization. After the 30 min purge, the mixture was heated to 115 °C. Samples were taken periodically until the reaction mixture was too viscous to extract samples or until 45 min had passed. The samples and final products were precipitated with methanol, allowed to settle, decanted, and then dried under vacuum at 70 °C for 24 h. The final copolymers were characterized by GPC for molecular weight and FT-IR for composition. For TBMA/S-20-PS, the yield was 2.4 g (22%) with $\bar{M}_n$ = 23.0 kg mol^{-1} and $\bar{M}_w/\bar{M}_n$ = 1.22 according to GPC relative to poly(styrene) standards in THF and F_{TBMA} = 0.13 according to FT-IR spectroscopy (TBMA carbonyl peak at 1720 cm^{-1} and styrene peak at 700 cm^{-1}).

Table 2. Chain Extension Formulations from Poly(*tert*-butyl methacrylate-*ran*-styrene) P(TBMA-*r*-S) Macroinitiators Done at Various temperatures in Bulk or Solvent

experiment ID[a]	[macroinitiator]$_0$ (mol L^{-1})	[monomer]$_0$ (mol L^{-1})	[solvent]$_0$ (mol L^{-1})	temp (°C)
TBMA/S-10-PS	0.026	8.75	0	115
TBMA/S-20-PS	0.015	8.75	0	115
TBMA/S-40-PS	0.013	8.75	0	115
TBMA/S-50-PS	0.014	8.75	0	115
TBMA/S-60-PS	0.009	8.75	0	115
TBMA/S-70-PS	0.009	8.75	0	115
TBMA/S-80-PS	0.008	8.75	0	115
TBMA/S-90-PS	0.007	8.75	0	115
TBMA/S-80-PTBS	1.247	1000	0	115
TBMA/S-80-PNIPAM	0.002	0.89	11.72[c]	105
TBMA/S-80-P(G/M/S)	0.008	1.541/2.19/0.431[b]	5.96[c]	85

[a] Experimental identification (ID) is given by TBMA/S-*XX*-*YY*, where TBMA = *tert*-butyl methacrylate and *XX* refers to the initial molar feed composition of TBMA. *YY* denotes the monomers which were used for the chain extension where PS = polystyrene, PTBS = poly(*tert*-butylstyrene), PNIPAM = poly(*N*-isopropylacrylamide), and P(G/M/S) = a ternary mixture of glycidyl methacrylate, methyl methacrylate, and styrene. All formulations had a relative mass ratio = $m_{\mathrm{macroinitiator}}/m_{\mathrm{styrene}}$ = 0.1. [b] [Monomer]$_0$ of a ternary mixture is denoted as follows: [GMA]$_0$/[MMA]$_0$/[S]$_0$. [c] TBMA/S-80-PNIPAM and TBMA/S-80-P(G/M/S) were polymerized in 1,4-dioxane.

Synthesis of Functional Block Copolymers: Poly(*tert*-butyl methacrylate-*random*-styrene) as Macroinitiator To Polymerize *tert*-Butylstyrene, *N*-Isopropylacrylamide, and Glycidyl Methacrylate/Methyl Methacrylate/Styrene Mixture. Previously synthesized *tert*-butyl methacrylate/styrene (TBMA/S-80) copolymer was used as a macroinitiator to reinitiate various fresh batches of monomer. These chain extensions were done in the same reactor with an identical setup and procedure as the previously described styrene chain extension. The solvent and polymerization temperatures used are illustrated in Scheme 1. The formulations for all chain extensions of TBMA/S-80 macroinitiator can be found in Table 2. Similar to the styrene chain extensions, previously purified NIPAM (3.07 g, 27.0 mmol), the macroinitiator TBMA/S-80 (0.51 g, 0.044 mmol, $\bar{M}_n$ = 14.2 kg mol^{-1}, $\bar{M}_w/\bar{M}_n$ = 1.30, and F_{TBMA} = 0.65), and 1,4-dioxane (25 mL) were mixed with a magnetic stirrer in a 100 mL three-neck round-bottom flask reactor. After the nitrogen purge, the mixture was heated to 105 °C, and samples were taken periodically until 100 min had passed. The samples and final products were precipitated using hexane, allowed to settle, decanted, and then dried under vacuum at 70 °C for 24 h. The final copolymers were characterized by GPC for molecular weight and ^{1}H NMR for composition. For TBMA/S-80-PNIPAM, the yield was 1.4 g (39%) with $\bar{M}_n = 17.8$ kg mol^{-1}, $\bar{M}_w/\bar{M}_n = 1.59$, and $F_{TBMA} = 0.43$ (^{1}H NMR spectroscopy: for TBMA, 9H, C$-$(CH_3)$_3$ = 1.49 ppm; for styrene, 5H, Ar, 7.5$-$7.1 ppm; and for NIPAM, CH$-$(CH_3)$_2$ = 5.60 ppm, C$H$$-$(CH$_3$)$_2$ = 4.16 ppm).

Characterization. Monomer conversion was determined by gravimetry. The molecular weight distributions were measured using gel permeation chromatography (GPC, Waters Breeze) with tetrahydrofuran (THF) as the mobile phase and a flow rate of 0.3 mL min^{-1}. The GPC unit was equipped with three Waters Styragel columns connected in series as follows: guard column (4.6 mm diameter and 30 mm length), HR1 (molecular weight measurement range of $10^2$$-$$5 \times 10^3$ g mol^{-1}), HR2 (molecular weight measurement range of $5 \times 10^2$$-$$2 \times 10^4$ g mol^{-1}), and HR4 (molecular weight measurement range of $5 \times 10^3$$-$$6 \times 10^5$ g mol^{-1}). The smaller diameter columns (4.6 mm diameter and 300 mm length) required lower flow rates and thus saved solvent. The columns were heated to 40 °C during the analysis. The molecular weights were determined using calibration via narrow molecular weight distribution poly(styrene) standards. 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 styrene-containing copolymers. Fourier transform infrared spectroscopy (FT-IR) (Spectrum BX, Perkin-Elmer) was used to determine the composition of TBMA in the copolymers by using the carbonyl peak at 1720 cm^{-1} as a marker for the concentration of TBMA in the copolymer while the peak at 700 cm^{-1} was used as the marker for the concentration of styrene in copolymer. To accurately determine the copolymer composition, a five-point calibration curve was constructed with mixtures of poly(TBMA) ($\bar{M}_n = 38.5$ kg mol^{-1}, $\bar{M}_w/\bar{M}_n = 1.1$) and poly(styrene) ($\bar{M}_n = 13.0$ kg mol^{-1}, $\bar{M}_w/\bar{M}_n = 1.1$) standards.

The TBMA-containing random copolymer (TBMA/S-80) was further analyzed by ^{31}P NMR spectroscopy to determine the fraction of the chains terminated with SG1. The spectrum was recorded in CDCl$_3$ using a 5 mm diameter Up NMR tube with 6000 scans being performed in a 200 MHz Varian Gemini 2000 spectrometer operating at 81 MHz. The spectrum was recorded using identical parameters to Charleux et al.[44] for comparison: flip angle of 10°, relaxation delay of 20 s, and suppression of the NOE. The NMR tube was carefully weighed and filled with polymer (TBMA/S-80; mass of polymer = 0.2434 g; $\bar{M}_n = 14.2$ kg/mol; after compensating for 13.3% residual monomer and solvent, the result was 1.84×10^{-5} mol of polymer: $\delta = 24.5$$-$$26.5$ ppm in CDCl$_3$) and diethyl phosphite as internal reference (0.0238 g; 1.72×10^{-4} mol; $\delta = 8.0$$-$$8.5$ ppm in CDCl$_3$). T_g's were determined using modulated DSC which was calibrated for temperature with indium standards and for heat flow using benzoic acid standards. Modulated DSC was performed in the temperature range of 90$-$150 °C using a triple scan cycle (heat/cool/heat—used to remove processing history) at a rate of 10 °C min^{-1}. The inflection method was used to determine the T_g values from the change in slope observed in the DSC traces. The Zetasizer (Malvern Instruments Ltd.) was equipped with a 50 mW green laser operating at 532 nm and was employed to analyze the particle size distribution (Z-average particle diameter) of the final water-soluble NIPAM-containing polymer. The sample was heated using Peltier elements in temperature steps of 0.5 °C with a 5 min equilibration time between temperature steps, and the scattered light was detected at 90° to the incident beam. Measurements were carried out using a 1.12×10^{-3} g/mL copolymer solution in a water solution with a pH of 7.

Results and Discussion

***tert*-Butyl Methacrylate/Styrene Copolymerization: Effect of Feed Composition on Copolymer Composition.** Since the nitroxide-mediated copolymerization for TBMA/S has not been studied using the BlocBuilder/SG1 initiating system, it was necessary to find first how feed composition controls the copolymer composition and ultimately polymerization kinetics. The results would then be useful for subsequent tailoring of composition for the desired application. The compositions of the copolymers were determined by Fourier transform infrared spectroscopy (FT-IR) using the TBMA carbonyl stretch at 1720 cm^{-1} and the styrene stretch at 700 cm^{-1} as markers (see Figures S2a and S2b in the Supporting Information). Table 3 indicates the compositions of the various TBMA/S random copolymers synthesized for various initial feed formulations. At low $f_{TBMA,0}$, the molar composition of TBMA in the copolymer, F_{TBMA}, was slightly richer than that of the feed while at higher initial TBMA feed concentrations ($f_{TBMA,0} > 0.35$), the copolymer composition became increasingly less rich in TBMA compared to the feed. This trend is consistent with previously reported observations for related *tert*-butyl acrylate/styrene nitroxide-mediated copolymerizations[24] and agrees well with TBMA/S conventional free radical copolymerization compositions measured using ^{1}H NMR spectroscopy.[45]

Extraction of the reactivity ratios was first done by linearization of the Mayo$-$Lewis equation[46] (e.g., the Fineman$-$Ross approach[47]) and by the Kelen$-$Tüdos approach.[48] Fineman$-$Ross and Kelen$-$Tüdos derivations and plots are shown in the Supporting Information and yield $r_{TBMA} = 0.13 \pm 0.02$ and $r_S = 0.43 \pm 0.07$ for the Fineman$-$Ross method and $r_{TBMA} = 0.27 \pm 0.02$ and $r_S = 0.59 \pm 0.05$ for the Kelen$-$Tüdos method. Although the Kelen-Tüdos method is an improvement over the Fineman$-$Ross method, it is still a linearization, and statistically a nonlinear least-squares fit to the Mayo$-$Lewis equation is probably the most sound method to determine the desired parameters.[49] Therefore, with the use of a commercially available software package (MatLab 2007), the reactivity ratios determined by the Kelen$-$Tüdos method were used as initial guesses for a nonlinear least-squares fitting of the data. At a confidence interval of 95%, the statistical fit to the data yielded $r_{TBMA} = 0.15 \pm 0.06$ and $r_S = 0.54 \pm 0.15$ (regression coefficient of $R^2 = 0.985$), which are not too dissimilar from those obtained by the other methods. The Mayo$-$Lewis plot is shown in Figure 1 using the reactivity ratios from the nonlinear least-squares fit with our experimental data. Even though the reactivity ratios obtained from one method to the other vary slightly, their effects on the Mayo plot are barely noticeable and in all cases fit the experimental data.

As a comparison, we found reactivity ratios for various TBMA/S binary conventional free radical copolymerizations available in the literature. du Sart et al. and Otsu et al. reported copolymer composition data for TBMA/S using conventional radical copolymerization at 80[45] and 60 °C,[50] respectively. du Sart et al. data reveal $r_{TBMA} = 0.60 \pm 0.02$, $r_S = 0.72 \pm 0.04$, and Otsu et al. data provide $r_{TBMA} = 0.59 \pm 0.03$, $r_S = 0.67 \pm 0.04$. Note that in both cases the copolymer composition agreed very closely with our data when $f_{TBMA,0} > 0.5$ (Figure 1). It is difficult to compare our data to others at $f_{TBMA,0} > 0.5$ since Otsu et al. only studied compositions up to $f_{TBMA,0} = 0.5$ and du Sart et al. reported

Table 3. Molecular Weight Characterization of Poly(*tert*-butyl methacrylate-*ran*-styrene) (P(TBMA-*r*-S)) Copolymers and Poly(*tert*-butyl methacrylate-*ran*-styrene)-*block*-Poly(X) (P(TBMA-*r*-S)-*b*-PX) (X = Styrene, *tert*-Butylstyrene, *N*-Isopropylacrylamide, and Glycidyl Methacrylate/Methyl Methacrylate/Styrene)

	macroinitiator				block copolymer			
experiment ID[a]	$f_{\mathrm{TBMA},0}$[c]	$\bar{M}_n$[b] (kg mol^{-1})	$\bar{M}_w/\bar{M}_n$[b]	F_{TBMA}[c]	$\bar{M}_n$[b] (kg mol^{-1})	$\bar{M}_w/\bar{M}_n$[b]	F_{TBMA}[c]	F_S, F_X[c]
TBMA/S-10-PS	0.10	4.5	1.29	0.16	14.0	1.76	0.04	0.96
TBMA/S-20-PS	0.20	6.7	1.21	0.22	23.0	1.22	0.13	0.87
TBMA/S-40-PS	0.41	8.0	1.28	0.35	25.2	1.40	0.18	0.82
TBMA/S-50-PS	0.49	8.8	1.29	0.42	27.2	1.35	0.17	0.83
TBMA/S-60-PS	0.60	12.4	1.28	0.49	35.7	1.34	0.35	0.64
TBMA/S-70-PS	0.70	13.9	1.29	0.55	43.1	1.35	0.42	0.58
TBMA/S-80-PS	0.80	14.2	1.30	0.65	45.7	1.37	0.28	0.72
TBMA/S-90-PS	0.92	15.6	1.31	0.67	17.9	1.32	0.48	0.52
TBMA/S-80-PTBS	0.80	14.2	1.30	0.65	81.0	1.33	0.16	0.10, 0.74
TBMA/S-80-PNIPAM	0.80	14.2	1.30	0.65	17.8	1.59	0.43	0.23, 0.34
TBMA/S-80-P(G/M/S)	0.80	14.2	1.30	0.65	32.9	1.41	0.22	0.19, 0.48

[a] Experimental identification (ID) is given by TBMA/S-*XX*-*YY*, where TBMA = *tert*-butyl methacrylate and *XX* refers to the initial molar feed composition of TBMA. *YY* denotes the monomers which were used for the chain extension where PS = poly(styrene), PTBS = poly(*tert*-butylstyrene), PNIPAM = poly(*N*-isopropylacrylamide), and P(G/M/S) = poly(glycidyl methacrylate-*ran*-methyl methacrylate-*ran*-styrene). All formulations had a relative mass ratio = $m_{\mathrm{macroinitiator}}/m_{\mathrm{styrene}} = 0.1$. All styrene and *tert*-butylstyrene chain extensions (TBMA/S-10-PS to TBMA/S-90-PS and TBMA/S-80-PTBS) were polymerized in bulk at 115 °C. TBMA/S-80-PNIPAM and TBMA/S-80-P(G/M/S) were polymerized in 1,4-dioxane at 105 and 85 °C, respectively. [b] Number-average molecular weight ($\bar{M}_n$) and polydispersity index ($\bar{M}_w/\bar{M}_n$) obtained by gel permeation chromatography (GPC) with linear poly(styrene) standards in tetrahydrofuran at 40 °C. [c] $f_{\mathrm{TBMA},0}$ is the initial molar feed composition of *tert*-butyl methacrylate, and F_{TBMA} is the final molar feed composition of *tert*-butyl methacrylate determined using Fourier transform infrared spectroscopy (FTIR). F_X is the final composition of TBS, NIPAM, or GMA determined by ^{1}H NMR.

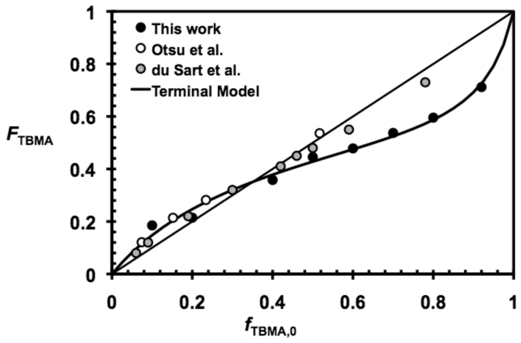


Figure 1. Mayo−Lewis plot of copolymer composition with respect to *tert*-butyl methacrylate, F_{TBMA}, versus monomer feed composition f_{TBMA} ($f_{\mathrm{TBMA}} \cong$ initial *tert*-butyl methacrylate monomer molar feed composition $f_{\mathrm{TBMA},0}$) using *tert*-butyl methacrylate and styrene reactivity ratios determined from nonlinear least-squares fitting of the Mayo−Lewis equation to the experimental data ($r_{\mathrm{TBMA}} = 0.15 \pm 0.06$ and $r_S = 0.54 \pm 0.15$). The experimental data for copolymerizations done in bulk at 90 °C using 10 mol % free nitroxide SG1 relative to BlocBuilder are indicated by the solid black circles while the solid dark line indicates the fit from the nonlinear least-squares to the Mayo−Lewis equation. The thin straight line indicates the azeotropic composition ($f_{\mathrm{TBMA}} = F_{\mathrm{TBMA}}$). The open circles refer to the data of Otsu et al., and the gray circles refer to the data of du Sart et al. for TBMA/S using conventional radical copolymerization at 60[50] and 80 °C,[45] respectively.

only two feed compositions above $f_{\mathrm{TBMA},0} = 0.5$. For controlled radical copolymerizations, the most similar system to ours was the *n*-butyl methacrylate/styrene system. Jianying et al., using NMP with TEMPO and benzoyl peroxide (BPO) as mediator/initiator at 125 °C, found $r_{n\text{-butyl methacrylate}} = 0.59$ and $r_{\mathrm{styrene}} = 1.27$,[51] while slightly different ratios were reported by Cuervo-Rodriguez et al. for *n*-butyl methacrylate/styrene copolymers made by NMP using a phenylethyl−TEMPO adduct as initiator at 125 °C ($r_{n\text{-butyl methacrylate}} = 0.42{-}0.46$, $r_{\mathrm{styrene}} = 0.53{-}0.57$).[52] In both cases, only four data points of *n*-butyl methacrylate initial feed composition ($f_{n\text{-BMA}}$) ranging from $f_{n\text{-BMA}} = 0.2$ to 0.7[49] and from $f_{n\text{-BMA}} = 0.2$ to 0.6[50] were used to determine the reactivity ratios. Regardless, the styrene reactivity ratio is higher than the TBMA reactivity ratio for NMP, in general agreement with that reported for conventional free radical copolymerizations and in *n*-butyl methacrylate/styrene copolymerizations using NMP.

Note that terminal models for the copolymerization fit the composition data well in Figure 1. However, such models are often grossly inadequate for determining copolymerization rates,[53−56] and thus a penultimate model is better for fitting kinetic data. Using our estimates for the monomer reactivity ratios r_{TBMA} and r_S from the nonlinear terminal model fit of the Mayo−Lewis relationship as fixed parameters, our kinetic data were fitted to an implicit penultimate unit effect (IPUE) model to yield the additional parameters describing penultimate effects: the radical reactivity ratios s_{TBMA} and s_S. Further details are given in the following section and the Supporting Information.

***tert*-Butyl Methacrylate/Styrene Copolymerization: Effect of Feed Composition on Kinetics.** The initial molar feed composition of TBMA ($f_{\mathrm{TBMA},0}$) not only influences the copolymer composition but also influences the polymerization kinetics. All experiments were carried out at 90 °C in bulk and formulated with an initial ratio of 10 mol % of SG1 free nitroxide relative to BlocBuilder ($r = [\mathrm{SG1}]_0/[\mathrm{BlocBuilder}]_0$). In all of the TBMA/S copolymerizations, experiments were designed to have a $\bar{M}_n = 25$ kg mol^{-1} at complete conversion (Table 1). The increase in conversion with time is depicted in Figure 2a by the semilogarithmic plot of $[\ln((1-x)^{-1})]$ (where x = conversion) versus time at various $f_{\mathrm{TBMA},0}$. The $\bar{M}_n$ versus x for the various copolymerizations are indicated in Figure 2b. At low conversion ($x < 0.1$), the short oligomers were relatively soluble in the precipitating solution (water/methanol) used to separate the monomer from polymer, and this likely resulted in the experimental $\bar{M}_n$ being greater than the theoretical $\bar{M}_n$. The GPC results were likely biased toward the larger nonsoluble polymers due to the loss of the oligomers. At high conversions, the $\bar{M}_n$ tended to plateau in some cases, indicating some irreversible termination reactions were occurring. In bulk the possibility of autoacceleration is considered, and polymer viscosity is monitored closely; therefore, the majority of termination would most likely result from β-hydrogen transfer to SG1[28] or intramolecular chain transfer.[29] The apparent rate constants, $\langle k_p\rangle[\mathrm{P}^\bullet]$, where $\langle k_p\rangle$ is defined as the average propagation rate constant and $[\mathrm{P}^\bullet]$ is the concentration of radicals that are propagating, were determined from the slopes of the

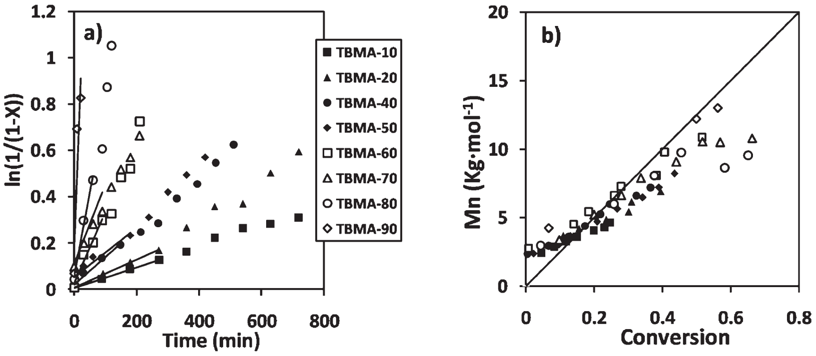


Figure 2. (a) Semilogarithmic plot of conversion ($\ln((1-x)^{-1})$) (x = conversion) versus time and (b) number-average molecular weight $\bar{M}_n$ versus x for copolymerizations of *tert*-butyl methacrylate/styrene (TBMA/S) with different initial compositions. The experiments using various TBMA initial molar feed compositions, $f_{\mathrm{TBMA},0}$, are represented symbolically as follows: $f_{\mathrm{TBMA},0} = 0.10$ (TBMA/S-10, ■), $f_{\mathrm{TBMA},0} = 0.20$ (TBMA/S-20, ▲), $f_{\mathrm{TBMA},0} = 0.40$ (TBMA/S-40, ●), $f_{\mathrm{TBMA},0} = 0.50$ (TBMA/S-50, ♦), $f_{\mathrm{TBMA},0} = 0.60$ (TBMA/S-60, □), $f_{\mathrm{TBMA},0} = 0.70$ (TBMA/S-70, △), $f_{\mathrm{TBMA},0} = 0.80$ (TBMA/S-80, ○), and $f_{\mathrm{TBMA},0} = 0.92$ (TBMA/S-90, ◇). The characterization data of TBMA/S-10 to TBMA/S-90 are shown in Table 3 under the heading titled “macroinitiator”.

plots in Figure 2a in the linear regions where $[\mathrm{P}^\bullet]$ is expected to remain relatively constant. These slopes can be related to the equilibrium between the dormant and the active chains as shown in eq 1.[57]

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

$\langle K\rangle$ is the average equilibrium constant equal to $[\mathrm{P}^\bullet]$ multiplied by the concentration of free nitroxide $[\mathrm{N}^\bullet]$ divided by the concentration of the dormant alkoxyamine-terminated species [P−N]. An average equilibrium constant is defined since the random copolymerization of two monomers could have equilibrium constants that depend on the nature of the monomer and the radical chain end. The overall polymerization rate can be defined by the rate of chain propagation which is defined by eq 2.

$$R_{\mathrm{P}} = -\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} = k_{\mathrm{p}}[\mathrm{P}^\bullet][\mathrm{M}] \tag{2}$$

where the propagating radical concentration, $[\mathrm{P}^\bullet]$, is controlled by eq 1. Early in the polymerization we can assume the initial concentration of free nitroxide $[\mathrm{N}^\bullet]_0$ is high and does not change significantly at this point so that $[\mathrm{N}^\bullet] = [\mathrm{N}^\bullet]_0$. Also, [P−N] is assumed approximately equal to the initial concentration of initiator ($[\mathrm{P{-}N}] = [\mathrm{BlocBuilder}]_0$).

Given the definition of $r = [\mathrm{SG1}]_0/[\mathrm{BlocBuilder}]_0$, eq 1 can be multiplied by $\langle k_{\mathrm{p}}\rangle$ to give the following:

$$\langle k_{\mathrm{p}}\rangle\langle K\rangle = \langle k_{\mathrm{p}}\rangle \frac{[\mathrm{P}^\bullet][\mathrm{SG1}^\bullet]_0}{[\mathrm{BlocBuilder}]_0} = \langle k_{\mathrm{p}}\rangle[\mathrm{P}^\bullet]r \tag{3}$$

As previously mentioned, the reported $\langle k_{\mathrm{p}}\rangle[\mathrm{P}^\bullet]$ for the various copolymerizations were taken during the early stages of polymerization, at low conversion, where a linear growth of $\bar{M}_n$ versus x was observed. Thus, eq 3 is applicable. Obviously, electron spin resonance (ESR) experiments would conclusively determine if the assumptions hold and future work in our group using ESR will be done to compare kinetic parameters.

As $f_{\mathrm{TBMA},0}$ increased, the $\langle k_{\mathrm{p}}\rangle\langle K\rangle$'s increased with $\langle k_{\mathrm{p}}\rangle\langle K\rangle = (7.4 \pm 0.03) \times 10^{-7}\ \mathrm{s}^{-1}$ at $f_{\mathrm{TBMA},0} = 0.10$ to $\langle k_{\mathrm{p}}\rangle\langle K\rangle = (5.4 \pm 0.9) \times 10^{-5}\ \mathrm{s}^{-1}$ at $f_{\mathrm{TBMA},0} = 0.92$ (Figure 3). Note that Figure 3 illustrates the controlling influence of adding just a small amount of styrene on $\langle k_{\mathrm{p}}\rangle\langle K\rangle$. Increasing f_{styrene} from 0.1 to 0.2 resulted in approximately a 5-fold decrease in the estimated $\langle k_{\mathrm{p}}\rangle\langle K\rangle$. The $\langle k_{\mathrm{p}}\rangle\langle K\rangle$ values at $f_{\mathrm{TBMA},0} = 0.10$ and at $f_{\mathrm{TBMA},0} = 0.92$ are bracketed well by $k_{\mathrm{p}}K$ of pure styrene at 90 °C ($k_{\mathrm{p}}K \approx 3.6 \times 10^{-7}\ \mathrm{s}^{-1}$)[58,59] and that of a structurally similar methacrylate to that of TBMA, methyl methacrylate (MMA), at 90 °C ($k_{\mathrm{p}}K \approx 1.6 \times 10^{-4}\ \mathrm{s}^{-1}$).[39] The homopropagation rate constant for TBMA ($k_{\mathrm{p,TBMA}}$) has been reported by Pascal et al.[60] and more recently by Roberts et al.[61] The $\langle k_{\mathrm{p}}\rangle\langle K\rangle$ increase with $f_{\mathrm{TBMA},0}$ may be in part be due to the higher k_{p} of TBMA ($k_{\mathrm{p,TBMA}} \approx 1.6 \times 10^3\ \mathrm{L\ mol\ s^{-1}}$)[61] compared to styrene ($k_{\mathrm{p,styrene}} \approx 9.0 \times 10^2\ \mathrm{L\ mol\ s^{-1}}$) at 90 °C. Further, K for methyl methacrylate is ∼2 orders of magnitude greater than that for styrene at 90 °C, and it is reasonable to assume that K for TBMA would be of the same order of magnitude as K for methyl methacrylate.[39] Extrapolation of the experimental data to TBMA homopolymerization (since K_{TBMA} for NMP is unavailable) suggests this is a reasonable approximation. Using the $\langle k_{\mathrm{p}}\rangle\langle K\rangle$ data points from $f_{\mathrm{TBMA},0} \leq 0.8$, extrapolation to $f_{\mathrm{TBMA},0} = 0$ gives $K_{\mathrm{TBMA}} \approx 2.6 \times 10^{-7}\ \mathrm{mol\ L^{-1}}$, which is about 2 times higher than that for MMA at the same temperature. The K_{TBMA} calculated from extrapolation was used to provide an estimate for additional kinetic parameters needed for an IPUE kinetic model fit.

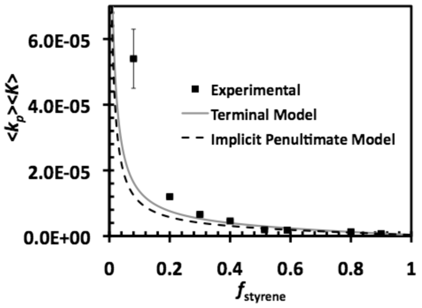


Figure 3. Product of the average propagation rate constant, $\langle k_{\mathrm{p}}\rangle$, with the average equilibrium constant, $\langle K\rangle$, $\langle k_{\mathrm{p}}\rangle\langle K\rangle$, for *tert*-butyl methacrylate/styrene (TBMA/S) copolymerizations at 90 °C in bulk versus initial molar feed composition of styrene ($f_{\mathrm{styrene},0}$). The experimental data are indicated by the full circles (■) with error bars derived from the standard error of the slope from the semilogarithmic kinetic plots, while the theoretical $\langle K\rangle\langle k_{\mathrm{p}}\rangle$ values were determined using the terminal model (solid line) and implicit penultimate unit effect model (dashed line) using appropriate literature values for homopropagation rate and equilibrium constants (see Supporting Information). Note that for this system it was assumed that $K_{\mathrm{TBMA}} \approx 2.6 \times 10^{-7}\ \mathrm{mol\ L^{-1}}$ from extrapolation of data points where $f_{\mathrm{styrene},0} \geq 0.2$.

Although copolymer composition can often be characterized by a terminal kinetic model as indicated earlier, the copolymerization kinetics frequently cannot be described adequately with such a simple model.[55] Often a penultimate model describes the kinetic behavior better for a copolymerization.[54,62] Charleux and co-workers developed an expression for the binary controlled radical polymerization parameters $\langle k_p \rangle \langle K \rangle$, assuming a terminal or an IPUE model, for monomers A and B in terms of f_A, f_B, r_A, r_B, s_A, s_B, individual propagation rate constants ($k_{p,A}$ and $k_{p,B}$) and equilibrium constants (K_A and K_B) (see eq 3 for the IPUE model). Fitting our data with such a model will be useful for further work in estimating a priori the copolymer composition and polymerization rates for TBMA/S nitroxide-mediated copolymerizations.

$$\langle k_p \rangle \langle K \rangle = \frac{r_A f_A{}^2 + 2 f_A f_B + r_B f_B{}^2}{\dfrac{r_A f_A}{\overline{k_{p,A}}\, K_A} + \dfrac{r_B f_B}{\overline{k_{p,B}}\, K_B}}$$

$$\overline{k_{p,A}} = k_{p,A} \frac{r_A f_A + f_B}{r_A f_A + f_B / s_A}; \quad \overline{k_{p,B}} = k_{p,B} \frac{r_B f_B + f_A}{r_B f_B + f_A / s_B} \qquad (4)$$

Since we did not have any values for K_{TBMA} presently, it was estimated, by extrapolation from the experimental data, that $K_{TBMA} \approx 2.6 \times 10^{-7}$ mol L^{-1}. Thus, a comparison of terminal versus penultimate models is possible given the above approximation for K_{TBMA} and the previously determined reactivity ratios r_{TBMA} and r_S, along with the literature values for propagation rate constants of TBMA and styrene and K_S. This permitted the determination of the radical reactivity ratios s_{TBMA} and s_S to be used for the IPUE model fit of the $\langle k_p \rangle \langle K \rangle$ data. As can be seen from Figure 3, the $\langle k_p \rangle \langle K \rangle$ fit as a function of $f_{TBMA,0}$ can be expressed by either a terminal or penultimate model, with a close fit to either model below $f_{TBMA,0} = 0.8$. At $f_{TBMA,0} > 0.8$, the polymerization is exceedingly rapid, and an estimate for $\langle k_p \rangle \langle K \rangle$ is subject to considerable uncertainty. Future experiments will use the IPUE parameters estimated here for use in fitting of data where the $\langle k_p \rangle \langle K \rangle$ changes very rapidly ($0.8 \le f_{TBMA,0} \le 0.9$). Also, direct estimates of K_{TBMA} from ESR measurements should improve prediction of copolymerization kinetics.

The molecular weight characterization of all copolymers (TBMA/S-10 to 90) is shown in Table 3. The TBMA/S copolymer $\bar{M}_n$ was plotted versus conversion (Figure 2b), and as the conversion increases, the plots exhibit a leveling of the $\bar{M}_n$ at higher conversions. This leveling off is much more apparent in cases where $f_{TBMA,0}$ was higher ($f_{TBMA,0} > 0.6$) compared to the copolymers with lower $f_{TBMA,0} < 0.5$. All of the GPC chromatograms indicated the distributions were monomodal. A more detailed analysis of the polymer "livingness" will be discussed in a following section. Two sets of chromatograms are shown with samples taken from polymerizations with greatly different TBMA feed content at different times during the polymerizations which indicate the monomodal nature of the TBMA/S copolymerizations (Figure 4).

Styrene Chain Extension from *tert*-Butyl Methacrylate/Styrene Macroinitiators. TBMA containing random copolymer macroinitiators (TBMA/S-10 to TBMA/S-92), synthesized previously using BlocBuilder initiator and additional SG1 free nitroxide, were used as macroinitiators to polymerize a fresh batch of styrene at 115 °C. To avoid excessive thermal initiation of styrene, a polymerization temperature below 120 °C[63] was selected for polymerization of the batch of pure styrene. This set of chain extensions would demonstrate whether these macroinitiators were significantly "living" enough to polymerize a second batch of a monomer which is fairly easy to control by NMP (e.g., styrene). Methacrylate/styrene copolymers synthesized by NMP exhibited signs of "livingness" by their ability to cleanly reinitiate a fresh batch of monomer successfully without a large fraction of uninitiated chains,[42,64] under appropriate conditions. Even with low amounts of styrene comonomer, the methacrylate-based macroinitiators possessed a high degree of livingness with living fractions typically greater than 75% and were predominantly terminated by a styryl-SG1 unit[64] that would facilitate addition of more styrene monomer to the chain end. The TBMA/S macroinitiators in the current study were polymerized with low target molecular weights and low conversions ($x < 40\%$) to avoid side reactions that would decrease livingness. ^{31}P NMR was performed and indicated that ~75% of the chains in a copolymer with a high TBMA content (TBMA/S-80) were SG1-capped and therefore capable of reinitiating a second batch of monomer relatively cleanly.

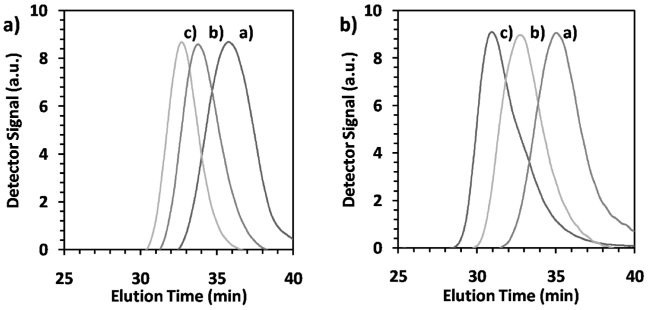


Figure 4. Gel permeation chromatograms of (part a) experiment TBMA/S-20 (initial molar feed fraction $f_{TBMA,0} = 0.20$) with samples taken at (a) 92 min, $X = 0.07$, $\bar{M}_n = 3.0$ kg mol^{-1}, $\bar{M}_w/\bar{M}_n = 1.24$; (b) 360 min, $X = 0.23$, $\bar{M}_n = 4.9$ kg mol^{-1}, $\bar{M}_w/\bar{M}_n = 1.26$; (c) 720 min, $X = 0.45$, $\bar{M}_n = 6.7$ kg mol^{-1}, $\bar{M}_w/\bar{M}_n = 1.21$; and (part b) experiment TBMA/S-80 ($f_{TBMA,0} = 0.80$) with samples taken at (a) 0 min, $X = 0.04$, $\bar{M}_n = 3.0$ kg mol^{-1}, $\bar{M}_w/\bar{M}_n = 1.22$; (b) 30 min, $X = 0.26$, $\bar{M}_n = 6.0$ kg mol^{-1}, $\bar{M}_w/\bar{M}_n = 1.26$; (c) 120 min, $X = 0.65$, $\bar{M}_n = 14.2$ kg mol^{-1}, $\bar{M}_w/\bar{M}_n = 1.30$. The reactions were all done in bulk at 90 °C.

The changes in $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and F_{TBMA} after the addition of styrene in experiments TBMA/S-10-PS to TBMA/S-92-PS are summarized in Table 3, while the shift in molecular weight as a function of elution time are illustrated from GPC chromatograms in Figure 5 for chain extensions of both high ($f_{TBMA,0} = 0.8$) and low ($f_{TBMA,0} = 0.2$) methacrylate containing macroinitiators and their resulting final copolymers. An increase in $\bar{M}_n$ from TBMA/S macroinitiators with $\bar{M}_n = 4.5-15.6$ kg mol^{-1} to TBMA/S-PS block copolymers with $\bar{M}_n = 14.0-45.7$ kg mol^{-1} was clearly observed. In addition to the change in molecular weight, a decrease in F_{TBMA} of the final products relative to the respective macroinitiator was apparent in all cases, indicating the addition of styrene monomer to the chains. The macroinitiators' $\bar{M}_w/\bar{M}_n$ varied from 1.21 to 1.31, and after chain extension, the copolymers had slightly broader molecular weight distributions with $\bar{M}_w/\bar{M}_n = 1.22-1.76$. Regardless of the macroinitiator F_{TBMA}, all final copolymers tended to undergo a slight broadening of molecular weight distributions after chain extension compared to the respective macroinitiators. In all cases, regardless of $f_{TBMA,0}$, the macroinitiators as well as the final copolymers' molecular weight distributions were monomodal and shifted steadily to higher molecular weight, thereby indicating that the macroinitiators were sufficiently "living" to reinitiate a fresh batch of styrene. These results suggest that

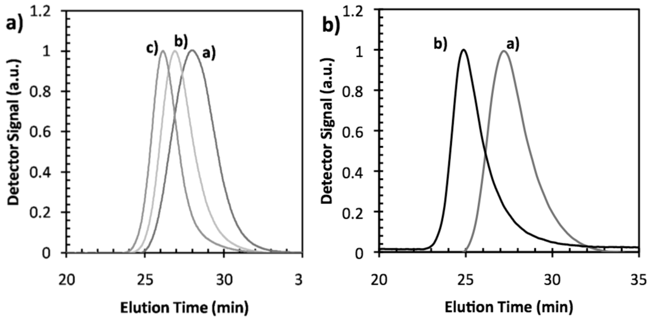


Figure 5. Gel permeation chromatograms for styrene chain extensions from two TBMA macroinitiators of different molar composition. Part a is the chain extension experiment TBMA/S-20-PS (Table 3) where the GPC traces belong to (a) TBMA/S-20 macroinitiator with $f_{\mathrm{TBMA},0}$ = 0.20 with $\bar{M}_n = 6.7$ kg mol^{-1} and $\bar{M}_w/\bar{M}_n$ = 1.21; (b) a sample taken at 15 min, $X_{\mathrm{styrene}} = 0.35$, $\bar{M}_n = 12.9$ kg mol^{-1}, and $\bar{M}_w/\bar{M}_n$ = 1.22; (c) a sample taken at 35 min, $X_{\mathrm{styrene}} = 0.61$, $\bar{M}_n = 23.0$ kg mol^{-1}, and $\bar{M}_w/\bar{M}_n$ = 1.22. Part b is the chain extension experiment TBMA/S-80-PS (Table 3) where the GPC traces belong to (a) TBMA/S-80 macroinitiator with $f_{\mathrm{TBMA},0}$ = 0.80 with $\bar{M}_n$ = 14.2 kg mol^{-1} and $\bar{M}_w/\bar{M}_n$ = 1.30; (b) the final sample taken at 45 min, $X_{\mathrm{styrene}} = 0.25$, $\bar{M}_n$ = 45.7 kg mol^{-1}, and $\bar{M}_w/\bar{M}_n$ = 1.37. The chain extensions were all done in bulk at 115 °C.

the synthesis of amphiphilic copolymers by NMP is possible with the use of a protected methacrylic acid species while maintaining relatively narrow and monomodal molecular weight distributions.

Functional Block Copolymer Formation by Chain Extension of *tert*-Butyl Methacrylate/Styrene Macroinitiators. After the "livingness" of the TBMA containing random copolymers was determined to be sufficient in reinitiating a second batch of styrene monomer, a wider variety of copolymers were designed as outlined in Scheme 1. The macroinitiator rich in TBMA (TBMA/S-80) was used to synthesize three functional block copolymers with narrow molecular weight distributions. The second batches of monomer consisted of (i) *tert*-butylstyrene (TBS), (ii) *N*-isopropylacrylamide (NIPAM), and (iii) a ternary mixture of epoxy functional glycidyl methacrylate (GMA), methyl methacrylate (MMA), and styrene. The changes in $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and F_{TBMA} after the addition of the second batch of monomer are summarized in Table 3, while the change in molecular weight distribution as a function of elution time are displayed in the GPC chromatograms in Figure 6.

Poly(*tert*-butyl methacrylate-*random*-styrene)-*block*-Poly(*tert*-butylstyrene) (Poly(TBMA-*r*-S)-Poly(TBS)). The *tert*-butyl group on the TBMA segment of the block copolymer can be cleaved to give rise to a carboxylic acid group which can be used in the production of nanoporous membranes.[65] Styrene is often used as the model matrix for these types of applications due to its rigidity and ease of polymerization. The use of *tert*-butylstyrene would result in a matrix with a higher glass transition temperature. The experiment that represented this chain extension was TBMA/S-80-PTBS, whose molecular weight characteristics are represented in Table 3. An increase in molecular weight and a slight broadening of $\bar{M}_w/\bar{M}_n$ was observed from the macroinitiator (TBMA/S-80, $\bar{M}_n = 14.2$ kg mol^{-1}, $\bar{M}_w/\bar{M}_n = 1.30$) to final product (TBMA/S-80-PTBS, $\bar{M}_n$ = 81.0 kg mol^{-1}, $\bar{M}_w/\bar{M}_n = 1.33$). In addition to the change in molecular weight, a new peak resulting from the *tert*-butyl group of the TBS segment was detected by ^{1}H NMR, indicating a decrease in F_{TBMA} of the final copolymer. The GPC chromatograms illustrate a monomodal shift from macroinitiator to final copolymer in Figure 6a. DSC measurements were performed to determine glass transition temperatures (T_g) for both TBMA/S-80-PTBS and TBMA/S-80-PS (see Supporting Information). A shift was observed from $T_g \approx 100$ °C for the styrene chain extended block copolymer to $T_g \approx 140$ °C for the TBS chain extended product. The T_g's measured match well with literature values for the corresponding homopolymers (poly(TBS) = 132 °C, poly(TBMA) = 107 °C, and PS = 95 °C).[66] Thus, chain extensions from a TBMA-rich macroinitiator with a batch of TBS can lead to well-defined copolymers with higher T_g's for the potential matrix material.

Poly(*tert*-butyl methacrylate-*random*-styrene)-*block*-Poly(*N*-isopropylacrylamide) (Poly(TBMA-*r*-S)-Poly(NIPAM)). PNIPAM has long been used as a temperature-responsive polymer that is of keen interest in many aqueous phase applications such as drug delivery.[67,68] These unique features are due to PNIPAM exhibiting a lower critical solution temperature (LCST) of 32 °C.[69] The same macroinitiator as was used for the styrene and *tert*-butylstyrene chain extensions (P(TBMA/S-80), $\bar{M}_n = 14.2$ kg mol^{-1}, $\bar{M}_w/\bar{M}_n$ = 1.30, and $F_{\mathrm{TBMA}} = 0.65$, Table 3) was used to initiate a fresh batch of NIPAM at 105 °C (experiment termed TBMA/S-80-PNIPAM, Table 3). An increase in molecular weight and a slight broadening in molecular weight distribution was observed after reinitiating with a fresh batch of NIPAM ($\bar{M}_n = 17.8$ kg mol^{-1}, $\bar{M}_w/\bar{M}_n = 1.59$). The GPC chromatograms show that even though the final copolymer was rather broad in terms of molecular weight distribution, a monomodal shift from macroinitiator to final copolymer was still observed (Figure 6b). ^{1}H NMR was employed to determine the composition of the final copolymer ($F_{\mathrm{TBMA}} = 0.43$) and provided evidence that the NIPAM was incorporated into the copolymer. Further evidence of incorporation could be attained by examining the aqueous phase behavior after conversion of the copolymer to a water-soluble form.

The final copolymer, entry TBMA/S-80-PNIPAM in Table 3, was then treated with acid to cleave the *tert*-butyl group giving a water-soluble poly(methacrylic acid-*random*-styrene)-*block*-poly(*N*-isopropylacrylamide) (P(MAA-*r*-S)-P(NIPAM)). The cleaving of the *tert*-butyl group was done in an identical fashion to that previously performed on poly(styrene)/*tert*-butyl acrylate block copolymers.[25] A 1.1×10^{-3} g mL^{-1} solution of the now water-soluble block copolymer in water was mixed and heated to observe any temperature-responsive behavior. The polymer solution was slightly cloudy at room temperature (due perhaps to the low fraction of styrene incorporated into the first block (Figure 7b, left side), and when heated, the sample went completely cloudy (Figure 7b, right side). Particle size analysis was used as an indicator for the phase transition from water solubility to phase-separated behavior. The particle diameter approximately quadrupled between 32 and 34 °C (Figure 7a). Several factors can modify this phase transition zone, for example, the fraction of methacrylic acid in the copolymer, the pH of the solution, or ionic strength.[70,71] The transition temperature is in agreement with that exhibited by other PNIPAM-containing copolymers, being around 32 °C.[69] These results show the potential versatility of NMP as water-soluble thermoresponsive copolymers can be synthesized from organo-soluble poly(TBMA/S) precursors. Further experiments are underway to determine how effective BlocBuilder is at controlling NIPAM polymerizations by NMP.

Poly(*tert*-butyl methacrylate-*random*-styrene)-*block*-Poly(glycidyl methacrylate-*random*-methyl methacrylate-*random*-styrene) (Poly(TBMA-*r*-S)-Poly(GMA/MMA/S)). P(TBMA/S-80) macroinitiator was also used to reinitiate a ternary batch

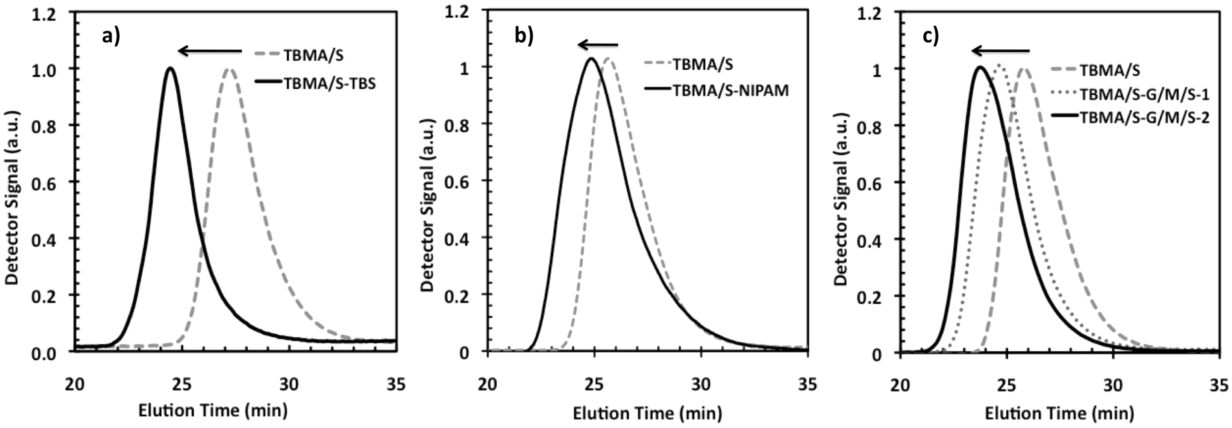


Figure 6. Gel permeation chromatograms for various chain extensions of TBMA macroinitiator with different batches of monomer. In all cases, the TBMA/S macroinitiator was TBMA/S-80 (Table 3, $F_{\mathrm{TBMA},0}$ = 0.65, $\bar{M}_n$ = 14.2 kg mol^{-1}, $\bar{M}_w/\bar{M}_n$ = 1.30). Part a shows the experiment TBMA/S-80-PTBS where the GPC traces belong to TBMA/S-80 macroinitiator (TBMA/S, dashed line) and chain extended TBMA/S-TBS (solid line) with X_{TBS} = 0.15, $\bar{M}_n$=81.0 kg mol^{-1}, and $\bar{M}_w/\bar{M}_n$=1.33. Part b shows the experiment TBMA/S-80-PNIPAM where the GPC traces belong to TBMA/S-80 macroinitiator (TBMA/S, dashed line) and TBMA/S-PNIPAM (solid line) final product with X_{NIPAM} = 0.05, $\bar{M}_n$ = 17.8 kg mol^{-1}, and $\bar{M}_w/\bar{M}_n$ = 1.59. Part c shows the experiment TBMA/S-80-P(G/M/S) where the GPC traces belong to TBMA/S-80 macroinitiator (TBMA/S, thicker dashed line), an intermediate sample TBMA/S-G/M/S-1 with $X_{\mathrm{GMA/MMA/S}}$ = 0.06, $\bar{M}_n$ = 19.6 kg mol^{-1}, $\bar{M}_w/\bar{M}_n$ =1.37 (finer dashed line) and TBMA/S-G/M/S-2 final product with $X_{\mathrm{GMA/MMA/S}}$ = 0.26, $\bar{M}_n$ = 32.9 kg mol^{-1}, $\bar{M}_w/\bar{M}_n$ =1.41 (solid line).

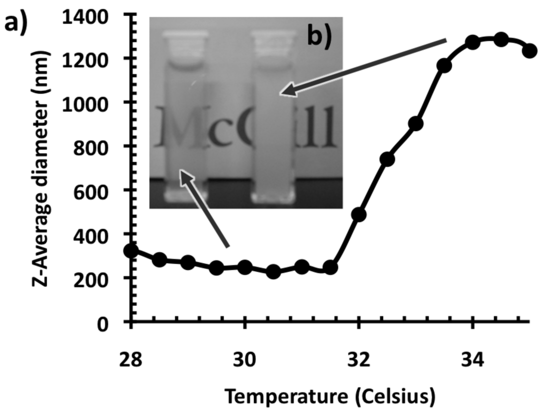


Figure 7. A poly(methacrylic acid-*ran*-styrene)-*block*-poly(*N*-isopropylacrylamide) (P(MAA/S)−PNIPAM) aqueous solution (concentration of 1.12 × 10^{-3} g mL^{-1}) was heated to determine its temperature responsiveness. The *Z*-average diameter versus temperature determined by dynamic light scattering (DLS) was measured in (a), indicating a sharp increase in size commencing at about 32 °C. (b) Photographs of two solutions with identical concentrations of P(MAA/S)−PNIPAM copolymer, with the sample on the left at room temperature (25 °C) while the sample on the right was heated to above 34 °C.

of GMA, MMA, and styrene (% molar ratio of 46/46/8, respectively). Similar methacrylate-rich, GMA-containing copolymers have recently been synthesized using various other methacrylic-based macroinitiators.[42] The resulting P(TBMA/S-80)−P(GMA/MMA/S) molecular weight characteristics are represented in Table 3. The macroinitiator (P(TBMA/S-80), $\bar{M}_n$=14.2 kg mol^{-1}, $\bar{M}_w/\bar{M}_n$=1.30) experienced an increase in molecular weight and a slight broadening of $\bar{M}_w/\bar{M}_n$ after chain extension with the GMA/MMA/S mixture (sample P(TBMA/S-80)−P(GMA/MMA/S), $\bar{M}_n$ = 32.9 kg mol^{-1}, $\bar{M}_w/\bar{M}_n$ = 1.41). Composition of the final copolymer was determined by ^{1}H NMR spectroscopy and indicated addition of GMA in the copolymer product. Similar to previously reported findings, the GPC chromatograms illustrated a monomodal shift from macroinitiator to final copolymer when using a mixture of methacrylates, which is challenging when incorporating GMA by NMP[42] (Figure 6c). The resulting block copolymer with TBMA and GMA is of interest after cleaving of the *tert*-butyl group on the TBMA block, leading to possible applications for optical wave guides[72] or water-soluble templates for immobilizing proteins.[73] Investigation of GMA copolymerizations using BlocBuilder are continuing to see how much GMA can be incorporated into the copolymer without any side reactions and maintaining a narrow molecular weight distribution.

Conclusion

This study aimed to discover the effects of *tert*-butyl methacrylate/styrene (TBMA/S) feed composition on the copolymer composition, copolymerization kinetics, and ability to initiate a fresh batch of a second monomer cleanly to produce various block copolymers. Copolymerizations were done using a BlocBuilder unimolecular initiator with additional SG1 free nitroxide (≈10 mol % relative to BlocBuilder) in bulk at 90 °C. Copolymer compositions indicated that TBMA/S random copolymer reactivity ratios r_{TBMA} and r_S were < 1 with $r_{\mathrm{TBMA}} < r_S$. The TBMA/S reactivity ratios ranged from $r_{\mathrm{TBMA}} = 0.13 \pm 0.02$, $r_S = 0.43 \pm 0.06$ by the Fineman−Ross method, $r_{\mathrm{TBMA}} = 0.27 \pm 0.02$, $r_S = 0.59 \pm 0.05$ for the Kelen−Tüdos method, and a $r_{\mathrm{TBMA}} = 0.15 \pm 0.06$, $r_S = 0.54 \pm 0.15$ by a nonlinear least-squares minimization fit to the Mayo−Lewis equation. Copolymer compositions agreed with those by conventional free radical copolymerization in comparable feed composition ranges. Fitting of the experimental $\langle k_p\rangle\langle K\rangle$ ($\langle k_p\rangle$ is the average propagation rate constant and $\langle K\rangle$ is the average equilibrium constant) with monmer feed composition for an implicit penultimate unit effect (IPUE) model, assuming the monomer reactivity ratios from the terminal model were fixed, along with literature k_p's and K_S and K_{TBMA} extrapolated from the experimental data, gave radical reactivity ratios $s_{\mathrm{TBMA}} = 0.4 \pm 0.3$ and $s_S = 0.9 \pm 0.4$.

As the TBMA initial feed composition increased, the apparent rate constants increased as well, which is not surprising, due to the difference in propagation rate constant of the respective monomers ($k_{p,\mathrm{TBMA}}$(90 °C) ≈ 1.6 × 10^3 L mol^{-1} s^{-1} and $k_{p,\mathrm{styrene}}$(90 °C) ≈ 9.0 × 10^2 L mol^{-1} s^{-1}).[53,61] As the feed composition of TBMA increased, $\langle k_p\rangle\langle K\rangle$ tended to increase, typical of methacrylate/styrene compositions. $\langle k_p\rangle\langle K\rangle$ values at 90 °C ranged from $(7.4 \pm 0.03) \times 10^{-7}$ s^{-1} at a feed composition $f_{\mathrm{TBMA},0}$ = $(0.1-5.4 \pm 0.9) \times 10^{-5}$ s^{-1} at a feed composition $f_{\mathrm{TBMA},0}$ = 0.92. These values approached that of pure styrene

NMP homopolymerization ($k_pK = 3.6 \times 10^{-7}$ s^{-1}) and that predicted for pure MMA homopolymerization ($k_pK = 1.6 \times 10^{-4}$ s^{-1}) at 90 °C. The estimated $\langle k_p \rangle \langle K \rangle$ could be fit to either a penultimate or terminal kinetic model over a fairly wide feed composition range. All of the copolymer molecular weight distributions remained monomodal and had reasonably low $\bar{M}_w/\bar{M}_n < 1.5$.

The resulting P(TBMA-*r*-S) copolymers were used as macroinitiators to reinitiate a fresh batch of styrene (S), *tert*-butylstyrene (TBS), *N*-isopropylacrylamide (NIPAM), and a ternary mixture of glycidyl methacrylate/methyl methacrylate/styrene (GMA/MMA/S). The resulting chain extended species maintained relatively narrow molecular weight distributions, regardless of the macroinitiator F_{TBMA}, and also retained monomodality. ^{31}P NMR showed that these *tert*-butyl methacrylate-rich precursor copolymers were substantially "living" with chain ends terminated with ~75% SG1 groups. Tunable mechanical properties of the second block were demonstrated by obtaining different T_g values for the styrene chain extension ($T_g \approx 100$ °C) compared to the *tert*-butylstyrene chain extension ($T_g \approx 140$ °C). Incorporation of potentially cross-linkable segments, using GMA, and water-soluble thermosensitive block copolymers, using NIPAM, was confirmed by ^{1}H NMR. The P(TBMA-*r*-S)-PNIPAM was converted to a water-dispersible species after cleavage of the *tert*-butyl protecting groups. The water-soluble copolymer exhibited a solubility transition between 32 and 34 °C in aqueous solution.

This work indicates that TBMA can be incorporated at relatively high levels into copolymers with styrene using NMP, and these copolymers can then be used as organo-soluble macroinitiator precursors for making organo- or water-soluble block copolymers with various functionalities. These findings show great promise toward the use of NMP to incorporate a wider range of methacrylic monomers for various applications.

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Supporting Information Available: FTIR spectra used to determine the composition of *tert*-butyl methacrylate in the random copolymer macroinitiators (Figure S1); methods for determining the reactivity ratios: (1) Fineman–Ross method in Figure S2a, (2) Kelen Tüdos method in Figure S2b, and (3) procedure used for least-squares minimization method fitting of parameters for the IPUE copolymerization kinetics model with MatLab 2007b and (4) the DSC traces in Figure S3 along with explanation for the T_g measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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