Nitroxide-Mediated Synthesis of Poly(poly(ethylene glycol) acrylate) (PPEGA) Comb-Like Homopolymers and Block Copolymers

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ABSTRACT: The kinetics of poly(ethylene glycol) acrylate (PEGA) nitroxide-mediated polymerization in bulk were studied at two temperatures (115 and 125 °C) and at initial molar ratios $r = 0.05-0.21$ of added free nitroxide (*N-tert*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide (SG1) relative to the unimolecular initiator 2-methyl-2-[*N-tert*-butyl-*N*-(diethoxylphosphoryl-2,2-(dimethylpropyl)aminooxy]propionic acid (BlocBuilder) ($r = [\mathrm{SG1}]_0/[\mathrm{BlocBuilder}]_0$). Bulk polymerizations were more controlled at 115 °C with $r = 0.10-0.21$ giving polymers with polydispersity indices ($\bar{M}_w/\bar{M}_n$) as low as 1.17 and a linear increase in number average molecular weight $\bar{M}_n$ with conversion up to about 50%. The k_pK values (k_p = propagation rate constant, K = equilibrium constant) for PEGA at 115 °C were 1.9×10^{-5} s^{-1} to 2.9×10^{-5} s^{-1} and at 125 °C were 6.7×10^{-5} to 8.3×10^{-5} s^{-1}. PEGA polymerizations in dimethylformamide (DMF) or anisole solution were most controlled when conducted in 25 wt % solutions, $r \sim 0.15$ and lower temperatures (95−115 °C) but side reactions were prevalent and control was not significantly better than in bulk. Chain extension of a comb-like poly(PEGA) (PPEGA, $\bar{M}_n$ = 8.1 kg/mol, $\bar{M}_w/\bar{M}_n$ = 1.20) with styrene in 50 wt % DMF solution at 115 °C to produce a PPEGA−poly(styrene) (PPEGA−PS) block copolymer indicated sufficient "livingness" of the PPEGA chain ends as observed by the steady increase in $\bar{M}_n$ and monomodal molecular weight distribution as determined by size exclusion chromatography although some broadening of the molecular weight distribution was evident ($\bar{M}_n$ = 62.3 kg/mol and $\bar{M}_w/\bar{M}_n$ = 1.53). ^{1}H NMR spectroscopy revealed resonances corresponding to the styrenic and PEGA segments and differential scanning calorimetry revealed two distinct glass transition temperatures T_g indicative of the PPEGA ($T_g \approx -70$ °C) and PS ($T_g \approx 98$ °C) segments.

Introduction

Comb-shaped polymers with hydrophilic poly(ethylene glycol) (PEG) side chains have received much attention for potential applications such as patterning protein arrays,[1,2] biomedical materials,[3−5] surfactants,[6−9] flocculants,[10,11] compatibilizers in polymer blending[12,13] and high energy density lithium batteries.[14,15] Extensive reviews of PEG side chain containing polymers have been published elsewhere in more detail.[16,17] Controlled-structure hydrophilic copolymers containing PEG have traditionally been synthesized by ionic polymerization or group transfer polymerization under strictly anhydrous conditions.[18−20] Recent advances however in controlled free radical polymerization chemistry have amplified the ease by which such block copolymers are made since they avoid rigorous and time-consuming solvent and monomer purification, protection of functional groups and air-free transfers required of ionic polymerization[21−26] and can even be done in aqueous media.[27]

The controlled radical polymerization of acrylate or methacrylate monomers with PEG side chains has been demonstrated using atom transfer radical polymerization (ATRP)[28−34] and reversible addition fragmentation transfer polymerization (RAFT).[35−39] Nitroxide-mediated polymerization (NMP) is desirable due to its simplicity, particularly when employing unimolecular initiators such as BlocBuilder (Arkema, Inc.)[40] that does not require any additional mediator to control polymerizations, compared to ATRP that requires catalyst removal and RAFT that often employs odorous thiol-based chain transfer agents. NMP has been used to copolymerize or polymerize initially styrenic and later acrylic or methacrylic monomers with PEG side chains. Oligo(ethylene glycol) styrene (3−5 ethylene glycol repeat units)[41] was polymerized using 2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane (TPPA) unimolecular alkoxyamine initiator with 5 mol % of 3-(1-phenylethoxy)-4-phenyl-3-azahexane (TPANO) free nitroxide relative to TPPA at 120 °C in anisole with number average molecular weights $\bar{M}_n$ ranging from 8.8−10.9 kg·mol^{-1} and low polydispersity indices $\bar{M}_w/\bar{M}_n$ ranging from 1.07−1.09 up to conversions of 45%. At higher conversions ~60% however, termination reactions started becoming prevalent with a higher molecular weight shoulder becoming noticeable in the molecular weight distributions. In addition to oligo(ethylene glycol) styrene, acrylate homopolymerizations that were not amenable to first-generation NMP mediators such as 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) were possible using second-generation nitroxides such as TPANO and TPPA. Oligo(ethylene glycol) acrylate (2−4 ethylene glycol repeat units)[41] was also polymerized using TPPA/TPANO in anisole at 110 °C with $\bar{M}_n \approx 9-10$ kg·mol^{-1} but slightly higher $\bar{M}_w/\bar{M}_n = 1.14-1.16$ after 6 h of polymerization and conversions up to about 40%.[42] Longer PEG side chains (8 EG repeat units) such as the monomer of interest in this study have however not been studied by NMP.

Another family of acyclic alkoxyamines based on *N-tert*-butyl-[*N*-1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide (SG1) mediator and related unimolecular initiators have been successfully applied for the controlled polymerization of acrylates such as *n*-butyl acrylate,[43,44] acrylic acid[45,46] and 2-hydroxyethyl acrylate.[47] More recently, the isobutyric acid functionalized alkoxyamine 2-methyl-2-[*N-tert*-butyl-*N*-(diethoxylphosphoryl-2,2-(dimethylpropyl)aminooxy]propionic acid (BlocBuilder) has also proven to be highly potent due to its high dissociation rate constant[48,49] and to be extremely versatile as a unimolecular initiator due to its water solubility when its carboxylic acid functionality was neutralized.[48,49] BlocBuilder has been effective not only for the controlled polymerization of acrylic systems

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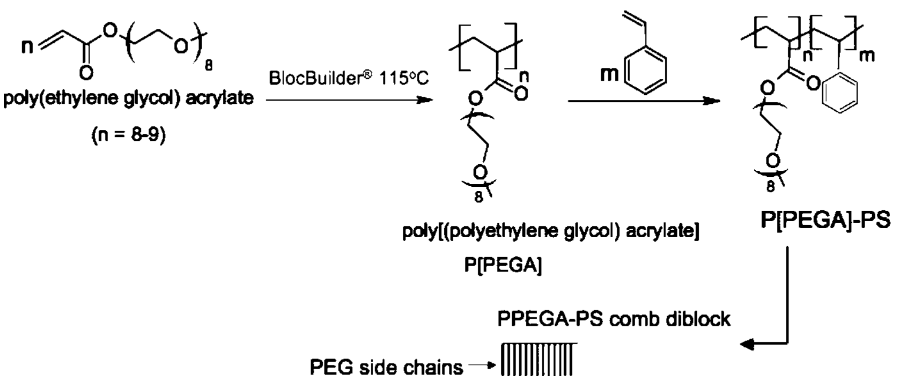
Scheme 1. Synthetic Route to Produce Poly[poly(ethylene glycol) acrylate] Homopolymer (PPEGA) Macroinitiator by Nitroxide Mediated Polymerization (NMP) Using BlocBuilder Unimolecular Initiator[a]



[a] The PPEGA macroinitiator was then used to initiate styrene in dimethylformamide (DMF) solution at 115 °C to yield the PPEGA−PS diblock.

Table 1. Experimental Conditions for Poly(ethylene glycol) Acrylate (PEGA) Initiated by BlocBuilder in Bulk at Various Levels of Additional SG1 Free Nitroxide and Temperature

expt. id	$[PEGA]_0$ (M)	$[BlocBuilder]_0$ (M)	$[SG1]_0$ (M)	r[a]	T (°C)	$\bar{M}_{n,target}$ (kg·mol^{-1})[b]
PPEGA-1	2.4	0.036	3.7×10^{-3}	0.10	115	30.2
PPEGA-2	2.4	0.035	3.7×10^{-3}	0.10	125	30.5
PPEGA-3	2.4	0.036	1.8×10^{-3}	0.05	115	30.2
PPEGA-4	2.4	0.036	1.9×10^{-3}	0.05	125	30.1
PPEGA-5	2.4	0.032	4.9×10^{-3}	0.16	115	33.8
PPEGA-6	2.4	0.035	7.4×10^{-3}	0.21	115	30.3
PPEGA-7	2.4	0.018	3.7×10^{-3}	0.21	115	61.1

[a] r = ratio of initial molar concentrations of SG1 free nitroxide relative to BlocBuilder unimolecular initiator = $[SG1]_0/[BlocBuilder]_0$. [b] Number average molecular weight ($\bar{M}_n$) and $\bar{M}_w/\bar{M}_n$ based on size exclusion chromatography (SEC) using linear poly(styrene) standards.

Table 2. Experimental Conditions for Poly(ethylene glycol) Acrylate (PEGA) Polymerization Initiated by BlocBuilder in Solution

expt id	solvent	$[PEGA]_0$[a] (M)	$[BlocBuilder]_0$[b] (M)	$[SG1]_0$[c] (M)	[solvent] (M)	r[d]	T (°C)
PPEGA-8	DMF[e]	1.1	0.017	0	6.9	0	115
PPEGA-9	DMF	1.1	0.017	9.1×10^{-4}	6.9	0.05	115
PPEGA-10	DMF	1.1	0.017	2.8×10^{-3}	6.9	0.17	115
PPEGA-11	DMF	0.6	8×10^{-3}	1.4×10^{-3}	9.9	0.17	105
PPEGA-12	anisole	0.6	9×10^{-3}	1.3×10^{-3}	7.0	0.15	105
PPEGA-13	anisole	0.6	8×10^{-3}	1.5×10^{-3}	7.0	0.18	95

[a] Initial concentration of poly(ethylene glycol) acrylate (PEGA) monomer. [b] BlocBuilder is the unimolecular initiator [*N*-*tert*-butyl-*N*-(diethoxyl-phosphoryl-2,2-(dimethylpropyl)-aminooxy] propionic acid. [c] SG1 is *N*-*tert*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide. [d] r is the molar concentration ratio of SG1 relative to BlocBuilder. [e] DMF is *N*,*N*-dimethylformamide.

Table 3. Experimental Conditions for Styrene Polymerization Initiated from Poly(poly(ethylene glycol) acrylate) (PPEGA) Macroinitiators in Solution at 115 °C

expt id	macroinitiator (MI) id	solvent	mass of MI (g)	mass of styrene (g)	mass of solvent (g)	mass of additional SG1[a] (g)
PPEGA−PS-1	PPEGA-5	dimethylformamide	2.0	20.0	21.9	0.011
PPEGA−PS-2	PPEGA-13	anisole	0.43	5.06	5.07	0

[a] SG1 is *N*-*tert*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide.

such as n-butyl acrylate,[50−53] acrylic acid/styrene copolymers[54−57] and *tert*-butyl acrylate[58,59] but also for methacrylates such as methyl methacrylate and methacrylic acid.[60−62] Recently, Nicolas et al. described the preparation of poly(methacrylates) with PEG side chains by polymerizing poly(ethylene glycol) methacrylate (PEGMA) with a small amount of styrene comonomer (~8.8 mol % styrene in the initial feed) using BlocBuilder and SG1 as the controlling system in bulk and ethanol solution at 78.5−80 °C.[63] Polymerizations with acceptable $\bar{M}_w/\bar{M}_n = 1.3-1.4$ and linear increases in $\bar{M}_n$ with conversion up to nearly 60% were achieved by performing the polymerization in more dilute (30 wt %) solutions. However, kinetic parameters were not reported in the communication that would be of interest for future design of homopolymers and amphiphilic copolymers involving acrylic or methacrylic PEG side chain polymers by NMP.

In particular, the kinetic data derived from this study will be used to develop comb-shaped polymers with PEG side chains so that when coupled to poly(styrene) blocks, the AB comb diblock can be used ultimately to template structures expected of ABC segmented triblocks after appropriate selective degradation.[64−67] We thus seek to optimize the polymerization of poly(ethylene glycol) acrylate (PEGA) monomer to make the comb block segment by determining appropriate BlocBuilder/free nitroxide SG1 ratios and temperatures to produce well-defined PPEGA. Further, the pseudo-"livingness" (defined loosely here as the linear increase in $\bar{M}_n$ with conversion and narrow molecular weight distribution) of the resulting PPEGA chain was tested by its use as an initiating species for the polymerization of a styrene block to produce the target PPEGA-*b*-poly(styrene) (PPEGA-*b*-PS) block copolymer. The synthetic route is summarized in Scheme 1 below.

Experimental Section

Materials. Basic alumina (Brockmann, type 1, 150 mesh), styrene (99.8%), anisole (anhydrous, 99.7%), poly(ethylene glycol)

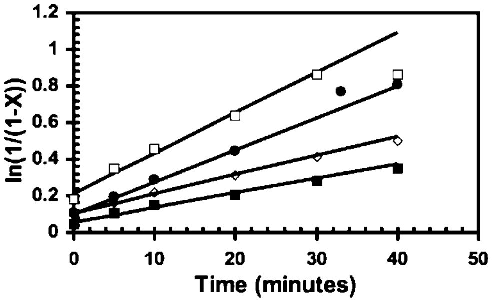


Figure 1. Scaled conversion (ln(1/(1 − X)) where X = conversion of poly(ethylene glycol) acrylate (PEGA) versus time for molar ratios r of free SG1 nitroxide relative to BlocBuilder (r = $[SG1]_0/[BlocBuilder]_0$) for bulk PEGA polymerizations at 115 °C. The solid lines are linear fits up to 20 min polymerization to calculate the apparent rate constant $k_p[P^\bullet]$ where k_p is the propagation rate constant and [P•] is the concentration of propagating macro-radicals. These experiments correspond to entries PPEGA-3 (r = 0.05 indicated by open squares, □), PPEGA-1 (r = 0.10 indicated by filled circles, ●), PPEGA-5 (r = 0.16 indicated by open diamonds, ◇) and PPEGA-6 (r = 0.21 indicated by filled squares, ■) in Table 1.

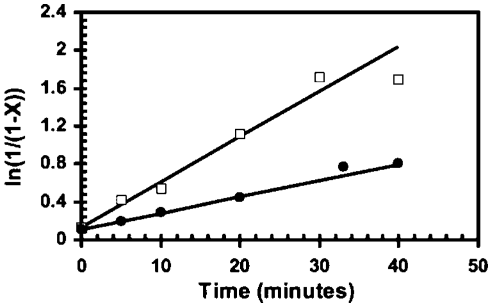


Figure 2. Scaled conversion (ln(1/(1 − X)) where X = conversion of poly(ethylene glycol) acrylate (PEGA) versus time for bulk polymerizations done at 115 °C (solid circles, ●) and 125 °C (open squares, □) using r = 0.10 molar ratio of free SG1 nitroxide relative to BlocBuilder (r = $[SG1]_0/[BlocBuilder]_0$) The solid lines are linear fits to the data taken at early points in the polymerization to calculate the apparent rate constant $k_p[P^\bullet]$ (k_p = propagation rate constant and $[P^\bullet]$ is the concentration of propagating macro-radicals. The series plotted correspond to entries PPEGA-1 and PPEGA-2 in Table 1.

acrylate (>99.5%) (PEGA, monomethyl terminated with 8 EG repeat units, number average molecular weight $\bar{M}_n \approx 450$ g·mol^{-1}) and calcium hydride (90−95% reagent grade) were purchased from Sigma-Aldrich. Methanol (99.8%), tetrahydrofuran (THF) (99.9%), methylene chloride (99.5%) and N,N dimethylformamide (DMF) (99.9%) were obtained from Fisher. Styrene and PEGA were purified by passing through a column of basic alumina mixed with 5 wt % calcium hydride and were then stored in sealed flasks under a head of nitrogen in a refrigerator until needed. Dialysis membrane tubing used to separate the poly(PEGA) (PPEGA) from the PEGA monomer was acquired from Spectrum Laboratories (MWCO = 3500 Da). 2-Methyl-2-[*N*-*tert*-butyl-*N*-(diethoxylphosphoryl-2,2-(dimethylpropyl)aminooxy]propionic acid, (99%, BlocBuilder) were purchased from Arkema and was used without further purification. *N*-*tert*-Butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide, also known as SG1, (>85%) was kindly donated by Noah Macy of Arkema and used as received.

Synthesis of Poly(poly(ethylene glycol) acrylate) (PPEGA). The syntheses were all performed in a 100 mL 3 neck round-bottom glass flask equipped with a condenser connected to a chiller unit (Neslab 740). The reactor was placed on top of a magnetic stirrer and was heated with a heating mantle connected to a controller and thermocouple. A sample synthesis in bulk for a target $\bar{M}_n$ of 30 kg·mol^{-1} (assuming that the monomer to initiator ratio gives the degree of polymerization at complete conversion) is given with reference to Table 1 for the experiment labeled PPEGA-1. BlocBuilder (0.25 g, 0.66 mmol) was added to the flask with the stirrer that was then sealed with a rubber septum with a needle placed to relieve the applied nitrogen purge. Previously purified PEGA (19.82 g, 0.042 mmol) and SG1 (0.020 g, 0.068 mmol) were injected into the reactor by syringe. Once stirring was started and the chilling unit was set to 0 °C, an ultra pure nitrogen flow was introduced to purge the system during monomer injection, as well as 15 min postinjection, at room temperature. The amount of BlocBuilder and PEGA monomer were calculated so that their target molecular weight was approximately 30 kg·mol^{-1} in all cases. Table 1 indicates all the formulations used for the bulk polymerizations while Table 2 indicates the formulations used for solution polymerizations in DMF or anisole. A 2 × 2 initial matrix of experiments was designed to find the key factors that would effect the bulk polymerization most strongly. The temperature (115 and 125 °C) and the initial molar concentration ratio of free SG1 in relation to BlocBuilder (termed r = $[SG1]_0/[BlocBuilder]_0$ = 0.05 and 0.10) were chosen as the variables. The reactor was then heated to 115 °C (or 125 °C) at a rate of about 10 °C·min^{-1} while maintaining a nitrogen purge. The time at which the reactor reached 115 °C (or 125 °C) was taken as the start of the reaction. Samples were taken with a syringe periodically. The samples were diluted in THF and directly characterized using size exclusion chromatography (SEC). Other samples without THF were taken to confirm the conversion using ^{1}H NMR spectroscopy. The bulk polymerizations were stopped when the solutions became too viscous to draw from the syringe. This typically occurred within 30 min of reaction. Solution polymerizations in DMF or anisole were longer and were carried out for 2−3 h typically (Table 2). Final samples were recovered using dialysis with a molecular porous membrane tubing with MWCO = 3500 in water to extract the unreacted monomer. Deionized water was freshly added every 8 h for three days to remove the monomer. The isolated polymer was then later dried in a vacuum oven for 24 h at 70 °C. For the specific example shown here, the final yield was 6.0 g (30% conversion) with number average molecular weight $\bar{M}_n$ = 10.7 kg·mol^{-1} and $\bar{M}_w/\bar{M}_n$ = 1.24 as determined by SEC relative to poly(styrene) standards.

Chain Extension of Poly(poly(ethylene glycol) acrylate) (PPEGA) with Styrene. The chain extension of PPEGA with a batch of styrene was performed in a 100 mL 3 neck round-bottom glass flask equipped with a condenser, thermal well and a magnetic Teflon stir bar in the same manner as was the case for the bulk PPEGA polymerizations. Table 3 lists the formulations for the chain extension experiments. The PPEGA with the BlocBuilder terminal group as initiator for the chain extension was added (2.00 g of sample PPEGA-5 which is shown in Table 1, 0.25 mmol, $\bar{M}_n$ = 8.1 kg/mol and $\bar{M}_w/\bar{M}_n$ = 1.20 relative to poly(styrene) standards by SEC) and the reactor was then sealed with a rubber septum. Styrene (21.92 g, 0.21 mol) and some additional SG1 free nitroxide (0.011 g, 0.037 mmol, 15 mol % relative to the BlocBuilder terminated PPEGA) were added to mediate the chain extension that was injected into the system using syringes. DMF (20.02 g) was then added to dissolve the styrene and PPEGA, which were immiscible without its inclusion. Once stirring was started and the chilling unit turned on, an ultra pure nitrogen flow was introduced to purge the system during monomer injection, as well as 15 min postinjection, at room temperature. The amounts of PPEGA and styrene monomer were added so that the target molecular weight of the block copolymer was approximately 90 kg·mol^{-1}. The reactor was then heated to 115 °C at a rate of about 10 °C·min^{-1} while maintaining a nitrogen purge. The time at which the reactor reached 115 °C was taken as the start of the reaction (t = 0). Samples were taken with a syringe periodically and were precipitated in hexane. The polymerization was stopped after 144 min. The samples were dried in a vacuum oven overnight at 60 °C and the conversion was determined gravimetrically. The final product yield was 10.8 g (45%) with number average molecular weight $\bar{M}_n$ = 62.3 kg·mol^{-1} and $\bar{M}_w/\bar{M}_n$ = 1.53 determined by SEC relative to poly(styrene) standards. The block copolymer composition was 23 mol % of EG (3.7 mol % relative to PEGA) measured by ^{1}H NMR spectroscopy in deuterated chloroform ($CDCl_3$) solvent.

Table 4. Kinetic Parameters for Poly(ethylene glycol) Acrylate (PEGA) Polymerized in Bulk at 115 and 125 °C with Various Ratios of Additional SG1 Free Nitroxide to BlocBuilder

expt id	$k_p[P^\bullet]^a$ (s^{-1})	k_pK (s^{-1})	r^b	temp (°C)	$\bar{M}_n{}^c$ (kg·mol^{-1})	$\bar{M}_w/\bar{M}_n{}^c$
PPEGA-3	$(3.7 \pm 0.2) \times 10^{-4}$	$(1.9 \pm 0.1) \times 10^{-5}$	0.052	115	12.0	1.29
PPEGA-1	$(2.8 \pm 0.1) \times 10^{-4}$	$(2.9 \pm 0.1) \times 10^{-5}$	0.104	115	10.7	1.24
PPEGA-5	$(1.8 \pm 0.1) \times 10^{-4}$	$(2.8 \pm 0.2) \times 10^{-5}$	0.156	115	8.1	1.20
PPEGA-6	$(1.3 \pm 0.2) \times 10^{-4}$	$(2.8 \pm 0.4) \times 10^{-5}$	0.207	115	7.7	1.17
PPEGA-4	$(1.3 \pm 0.3) \times 10^{-3}$	$(6.7 \pm 1.6) \times 10^{-5}$	0.052	125	11.3	1.80
PPEGA-2	$(8.0 \pm 0.7) \times 10^{-4}$	$(8.3 \pm 0.7) \times 10^{-5}$	0.104	125	11.6	1.61
PPEGA-8	$(1.5 \pm 0.2) \times 10^{-4}$	$(3.1 \pm 0.4) \times 10^{-5}$	0.207	115	12.5	1.24

[a] Error bars for apparent rate constants $k_p[P^\bullet]$ were determined from standard error in the slope for fits in the linear regions of the semilogarithmic kinetic plots of $\ln[1/(1 - X)]$ (where X = monomer conversion) versus time. [b] r is the molar ratio of SG1 free nitroxide (*N*-*tert*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide) added initially to that of BlocBuilder ([*N*-*tert*-butyl-*N*-(diethoxylphosphoryl-2,2-(dimethylpropyl)-aminooxy]propionic acid) added initially such that $r = [\mathrm{SG1}]_0/[\mathrm{BlocBuilder}]_0$. [c] Number average molecular weight $\bar{M}_n$ and polydispersity index $\bar{M}_w/\bar{M}_n$ was determined by size exclusion chromatography (SEC) using linear poly(styrene) standards in tetrahydrofuran solvent.

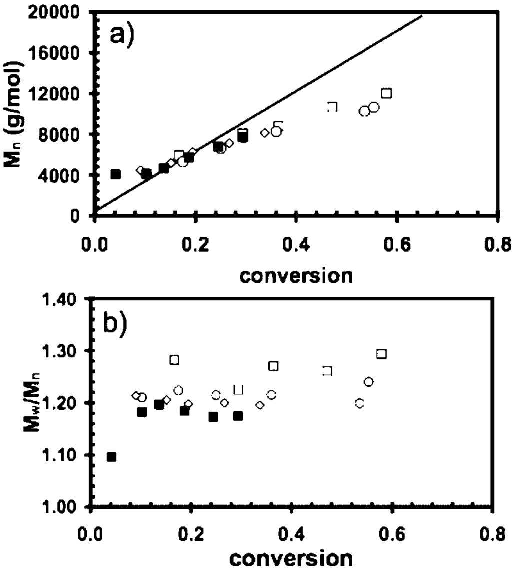


Figure 3. (a) Number average molecular weight $\bar{M}_n$ versus poly(ethylene glycol) acrylate (PEGA) conversion for polymerizations initiated by BlocBuilder at various initial levels of free nitroxide relative to BlocBuilder ($r = [\mathrm{SG1}]_0/[\mathrm{BlocBuilder}]_0$) at 115 °C ($r$ = 0.05 (□), 0.10 (○), 0.16 (■) and 0.21 (◇)) and (b) polydispersity index ($\bar{M}_w/\bar{M}_n$) versus conversion for the same samples shown in part a.

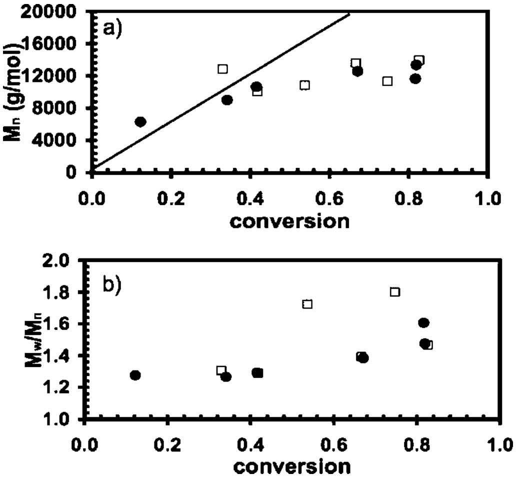


Figure 4. a) Number average molecular weight $\bar{M}_n$ versus poly(ethylene glycol) acrylate (PEGA) conversion for bulk polymerizations initiated by BlocBuilder at two levels of SG1 free nitroxide relative to BlocBuilder ($r = [\mathrm{SG1}]_0/[\mathrm{BlocBuilder}]_0$) ($r$ = 0.052 indicated by open squares (□) and r = 0.104 indicated by filled circles (●)) at 125 °C and b) polydispersity index ($\bar{M}_w/\bar{M}_n$) versus conversion for the same samples shown in part a.

Solution polymerization in anisole was done similarly except that no additional SG1 was used when polymerizing the batch of styrene.

Characterization of Molecular Weight and Conversion by Size Exclusion Chromatography (SEC). The molecular weight distribution was measured using size exclusion chromatography (SEC, Waters Breeze) with tetrahydrofuran (THF) as the mobile phase. The polymers and copolymers were soluble in organic solvents and therefore did not need further treatment prior to SEC analysis. A mobile phase flow rate of 0.3 mL·min^{-1} was applied and the SEC unit was equipped with 3 Waters Styragel columns connected in series as follows: HR1 (molecular weight measurement range of 10^2 to 5×10^3 g·mol^{-1}), HR2 (molecular weight measurement range of 5×10^2 to 2×10^4 g·mol^{-1} and HR4 (molecular weight measurement range of 5×10^3 to 6×10^5 g·mol^{-1}). Note that the lower flow rate was due to smaller diameter columns offered by the manufacturer (4.6 mm diameter and 300 mm length) than that usually used in order to save solvent. A guard column (4.6 mm diameter and 30 mm length) was also used. The columns were heated to 40 °C during the analysis. The molecular weights were determined using calibration against narrow molecular weight distribution poly(styrene) standards. The SEC unit was equipped with both ultraviolet (UV 2487 set to a wavelength of 255 nm to detect the aromatic rings in the poly(styrene) containing copolymers) and differential refractive index (RI 2410) detectors. The SEC was also used to determine the overall monomer conversion for the PEGA homopolymerizations, by comparing the areas of the monomer to the polymer ratio in the sample. Such a technique has been used previously for similar systems where SEC could detect the macro-monomer.[68,69]

Characterization of PEGA Conversion and Block Copolymer Composition by Nuclear Magnetic Resonance. ^{1}H NMR (200 MHz Varian Gemini 2000) with $CDCl_3$ solvent (Cambridge Isotope Laboratories Inc.) was used to verify the overall monomer conversion as well as the final composition of the coupled poly(styrene)-PPEGA copolymer product. After placing the samples with solvent in 5 mm Up NMR tubes, the samples were injected, shimmed and scanned 32 times. To determine the conversion of PEGA, the resonances of the vinylic protons (δ = 5.7−6.3 ppm) were compared to that of the PEG side chain (δ = 3.6 ppm) or the terminal CH_3 group of the PEG chain (δ = 3.3 ppm). To determine the composition of the block copolymer, the resonances corresponding to the PEG side chains (δ = 3.6 ppm) of the PPEGA were compared to the resonances of the aromatic protons from the styrene groups (δ = 6.5−7.1 ppm). The composition of the PPEGA-*b*-PS block copolymer was determined by comparing the aromatic protons corresponding to the styrene monomer at δ = 6−7 ppm with the ethylenic protons of the side chain CH_2CH_2O repeat units corresponding to the PEGA monomer at δ = 3.6 ppm. ^{1}H NMR in $CDCl_3$: (δ = 6.5−7.1 ppm, aromatic, C_6H_5), (δ = 4.2 ppm, 2H, COO-CH_2-), (δ = 3.6 ppm, 4H, CH_2CH_2O), (δ = 1.4−1.9 ppm, aliphatic backbone).

Characterization of Block Copolymer Thermal Transitions by Differential Scanning Calorimetry. Differential scanning calorimetry (DSC) was performed on the PPEGA−PS block copolymer to confirm if two distinct glass transition temperatures corresponding to each of the segments were present. A TA

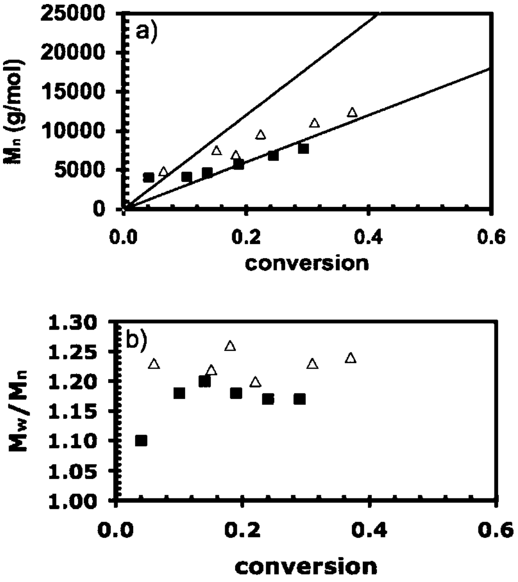


Figure 5. Number average molecular weight ($\bar{M}_n$) versus conversion for different target molecular weights ($\bar{M}_{n,target}$ = 30 kg·mol^{-1} indicated by filled squares (■) and $\bar{M}_{n,target}$ = 60 kg·mol^{-1} indicated by open triangles (△)) using $r = 0.21$ free SG1 nitroxide relative to BlocBuilder and 115 °C in bulk. The solid lines are linear fits to the theoretical target molecular weight that the data would follow if the polymerizations were pseudo-"living". The experiments shown correspond to entries PPEGA-6 and PPEGA-7 in Table 1.

Instruments (Q1000) DSC was operated in temperature-modulated mode in the range from −90 to 150 °C. The DSC was calibrated for temperature and heat flow with indium and benzoic acid standards. After equilibrating at −90 °C and holding for 5 min isothermally, modulation at ± 1.27 °C every 60 s was initiated while ramping at 2 °C·min^{-1} up to 150 °C and then held isothermally for 5 min. This first cycle was used to eliminate any residual thermal history. The DSC was then quenched to −90 °C and the cycle repeated at the same temperature oscillation of ± 1.27 °C every 60 s and ramping rate of 2 °C·min^{-1}. The second cycle was then used to determine the glass transition temperatures of the block copolymer and reported as the midpoint of the transition. Three tangent lines were drawn with the first and second lines corresponding to the slope before (onset) and after the transition region (offset) whereas the third tangent line was drawn that corresponded to the slope in the transition region (midpoint). The DSC measurement of the glass transition temperature (T_g) was found by using the onset method, which is defined as the midpoint of the intersection between the onset and the midpoint with the offset and the midpoint tangent lines.

Results and Discussion

Kinetics of Poly(ethylene glycol) Acrylate (PEGA) Bulk Nitroxide-Mediated Polymerization. Table 1 shows the initial compositions and parameters used in the polymerizations for the first part of this work: the bulk polymerization of PEGA with BlocBuilder and additional free nitroxide SG1. Specifically, the temperature and SG1 concentration in relation to BlocBuilder were optimized to find the best conditions to obtain pseudo-"living" polymerization that is defined here as the linear increase in number average molecular weight as a function of conversion with relatively narrow molecular weight distributions. Note this definition is not for a classical "living" system as defined by Szwarc[70] where termination and transfer processes are absent from the polymerization. In our study, the radical polymerizations suffer inevitably from termination reactions but we wish to obtain polymerizations that are controlled and exhibit nearly the same outward characteristics of truly "living" polymerizations. The estimation of the kinetic parameters was done by plotting ln(1/(1 − X)) (X = monomer conversion) versus time and determining the slopes in the linear region. Such plots are shown in Figures 1 and 2 at various initial SG1 free nitroxide concentrations relative to initiator and temperatures. The slopes from such plots are equal to $k_p[P^\bullet]$ where k_p is the propagation rate constant and $[P^\bullet]$ is the concentration of propagating macroradicals. In each experiment, more kinetic information can be obtained given the expression for the equilibrium between dormant and active chains. Equation 1 gives the equilibrium constant K which is defined as:

$$K = \frac{[P^\bullet][SG1]}{[P-SG1]} \tag{1}$$

where [SG1] is equal to the concentration of free nitroxide, $[P^\bullet]$ is the concentration of propagating macro-radicals and [P−SG1] is the concentration of SG1-polymer capped species. Multiplying Equation 1 by the propagation rate constant (k_p) gives the following expression.

$$k_pK = k_p\frac{[P^\bullet][SG1]}{[P-SG1]} \tag{2}$$

Since the initial concentration of free nitroxide $[SG1]_0$ is high, then [SG1] will not change much and thus [SG1] ≈ $[SG1]_0$ and if the polymerization is also assumed to be pseudo-"living", then [P−SG1] can be substituted by the initial concentration of BlocBuilder initiator ([P−SG1] = $[\text{BlocBuilder}]_0$). Obviously electron spin resonance (ESR) measurements would conclusively show if these assumptions strictly hold. However, if plots of $\bar{M}_n$ versus conversion remain sufficiently linear in the conversion range studied, then these assumptions would be satisfactory in estimating kinetic parameters when eq 2 is recast as eq 3.

$$k_pK \cong k_p\frac{[P^\bullet][SG1]_0}{[\text{BlocBuilder}]_0} = k_p[P^\bullet]r \tag{3}$$

Note that in eq 3 the parameter $r = [SG1]_0/[\text{BlocBuilder}]_0$ is defined as the initial molar ratio of free nitroxide to that of the BlocBuilder initiator. For this work, representative k_pK values were determined from bulk experiments utilizing several different r values and are presented in Table 4 as a function of added free nitroxide and temperature.

The k_pK values for PEGA bulk polymerization listed in Table 4 can be compared to other acrylic monomers. For PEGA polymerized at 115 °C, k_pK was in the range of 1.9×10^{-5} s^{-1} to 2.9×10^{-5} s^{-1}. When compared to other acrylic monomers such as *tert*-butyl acrylate (k_pK(115 °C) = 3.0×10^{-6} s^{-1}),[59] n-butyl acrylate (k_pK(120 °C) = 1.8×10^{-5} s^{-1}),[50] acrylic acid (k_pK(120 °C) = 1.1×10^{-5} s^{-1} to 1.8×10^{-5} s^{-1})[44] and hydroxyethyl acrylate (k_pK(120 °C) = 2.6×10^{-5} s^{-1}),[46] the k_pK of PPEGA is similar to all except *tert*-butyl acrylate which is lower as expected since its k_p is approximately half of that compared to n-butyl acrylate and acrylic acid.[74] At the higher temperature of 125 °C, k_pK values for PEGA ranged from $(6.7 \pm 1.6) \times 10^{-5}$ s^{-1} to $(8.3 \pm 0.7) \times 10^{-5}$ s^{-1} for the two different r values examined. Such an increase in k_pK over the 10 °C temperature range studied is not implausible assuming that the kinetics obeys Arrhenius type temperature dependence. However, the k_pK at 125 °C, particularly for the lower r value, should be treated carefully since the polymerization appears to be out of control and the assumptions involved in eq 3 may no longer be applicable.

Effect of Free Nitroxide and Temperature on $\bar{M}_n$ Evolution for Bulk PEGA Polymerizations. After performing the initial series of experiments examining two levels of temperature (115 and 125 °C) and two levels of free nitroxide relative to BlocBuilder (r = 0.05 and 0.10), we observed that a lower polymerization temperature and a higher initial free SG1

Table 5. Summary of Poly(ethylene glycol) Acrylate (PEGA) Polymerizations Initiated by BlocBuilder in Solution

expt id	solvent	[solvent] (M)	r^a	T (°C)	$\bar{M}_n$ (kg·mol^{-1})^b	$\bar{M}_w/\bar{M}_n{}^b$	t (min)^c	X^d
PPEGA-8	DMF^e	7.0	0	115	11.3	1.33	60	0.84
PPEGA-9	DMF	7.0	0.05	115	11.6	1.37	60	0.83
PPEGA-10	DMF	7.0	0.15	115	11.3	1.31	80	0.79
PPEGA-11	DMF	10.0	0.15	105	8.1	1.21	150	0.50
PPEGA-12	anisole	7.0	0.15	105	9.1	1.19	145	0.42
PPEGA-13	anisole	7.0	0.15	95	8.9	1.16	420	0.46

[a] r is the molar ratio of SG1 free nitroxide (*N*-*tert*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide) added initially to that of BlocBuilder([*N*-*tert*-butyl-*N*-(diethoxyl-phosphoryl-2,2-(dimethylpropyl)-aminooxy] propionic acid) added initially such that $r = [\mathrm{SG1}]_0/[\mathrm{BlocBuilder}]_0$. [b] Number average molecular weight $\bar{M}_n$ and polydispersity index $\bar{M}_w/\bar{M}_n$ was determined by size exclusion chromatography (SEC) using linear poly(styrene) standards in tetrahydrofuran solvent. [c] t was the polymerization time. [d] X was the conversion of monomer at the given polymerization time. [e] DMF is *N*,*N*-dimethylformamide solvent.

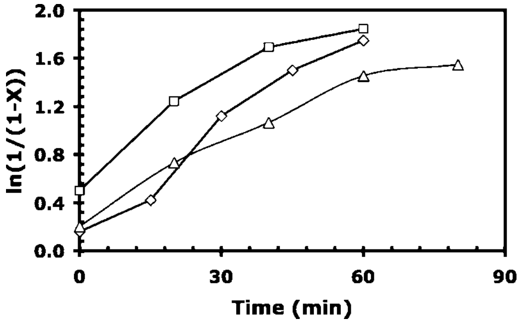


Figure 6. Plot of scaled conversion ($\ln(1/(1 - X))$ where X = monomer conversion) versus polymerization time for poly(ethylene glycol) acrylate (PEGA) polymerizations in 50 wt % dimethylformamide (DMF) solution at 115 °C at various initial molar ratios of SG1 free nitroxide relative to BlocBuilder initiator (r). Open squares (□) indicate the polymerization with $r = 0$, open diamonds (◇) indicate polymerizations with $r = 0.05$, and open triangles (△) indicate polymerizations with $r = 0.15$. In all cases, the monomer-to-initiator ratio was chosen so that the number average molecular weight was 30 kg·mol^{-1} at full conversion.

nitroxide concentration produced polymers with narrower and monomodal molecular weight distributions. We then examined in more detail the effect of varying r and temperature on the molecular weight distribution. Figures 3 and 4 show how the polymer $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ versus conversion vary with different r values at a fixed temperature of 115 °C and as function of temperature for a given r value, respectively, for the bulk PEGA polymerizations. In both cases, the monomer-to-initiator ratio targeting an approximate $\bar{M}_n$ of 30 kg·mol^{-1} based on the monomer-to-initiator ratio at full conversion was applied.

At 115 °C, the $\bar{M}_n$ versus conversion plot was linear up to about 40% conversion but begins to diverge from the theoretical line at higher conversions, regardless of the concentration of free nitroxide (Figure 3a). At higher conversions, exotherms occurred in some cases and $\bar{M}_w/\bar{M}_n$ began to increase, particularly when less additional SG1 free nitroxide was used (Figure 3b). Similar observations were made for bulk polymerizations of poly(ethylene glycol) methacrylate/styrene random copolymerizations (8.8 mol % styrene in the initial feed) at high conversion where loss of control was observed at 60% conversion with $\bar{M}_w/\bar{M}_n$ increasing to 2.2.[63] The slight divergence could be due to the increased effect of termination reactions or chain transfer reactions such as hydrogen abstraction which is common in conventional radical polymerization of poly(ethylene glycol) acrylate[71,72] and controlled radical polymerizations of different acrylates.[46,73]

Generally, with increasing initial SG1 added for polymerizations done at 115 °C, the $\bar{M}_w/\bar{M}_n$ decreased. For example, $\bar{M}_w/\bar{M}_n$ decreased from 1.29 after 30 min polymerization ($\bar{M}_n$ = 12.0 kg·mol^{-1}) for the experiment done at $r = 0.05$ to as low as 1.17 for the experiment done at $r = 0.21$ ($\bar{M}_n$ = 7.7 kg·mol^{-1}) after an equivalent polymerization time of 30 min. Also at the initial polymerization time at the lowest r values studied, some polymer was already formed, indicating that the polymerization was starting to occur at slightly lower temperatures than 115 °C. Thus, in bulk, more initial free nitroxide resulted in slower and more controlled polymerizations due to shifting of the equilibrium of the propagating macro-radicals to the dormant state more often, as expected.

At the higher temperature of 125 °C, $\bar{M}_w/\bar{M}_n > 1.5$ at both of the r's initially studied (Figure 4) and was much higher compared to the polymerizations done at 115 °C. For polymerizations done at the higher temperature of 125 °C, a similar decrease in $\bar{M}_w/\bar{M}_n$ was observed with more initial free nitroxide added as was the case for polymerizations at 115 °C but the molecular weight distributions remained relatively broad with $\bar{M}_w/\bar{M}_n > 1.5$. At 125 °C, there was obviously more of a plateau in $\bar{M}_n$ at the higher conversions measured in the $\bar{M}_n$ versus conversion plot, indicating that termination reactions become more predominant at the higher polymerization temperature (Figure 4a). This loss of control is even more obvious in the plot of $\bar{M}_w/\bar{M}_n$ versus conversion shown in Figure 4b) where $\bar{M}_w/\bar{M}_n$ oscillates approximately between 1.4−1.8. The $\bar{M}_w/\bar{M}_n$ steadily increased with conversion for either r value used. Thus, higher concentrations of free nitroxide would be likely required for polymerizations done at 125 °C to achieve the same degree of control of molecular weight distribution as observed for polymerizations done at 115 °C in bulk. The polymers produced at the higher r values at the lower temperature in bulk were subsequently chosen as macroinitiators to test the ability of the PPEGA to initiate the polymerization of a second batch of styrene monomer. These results also prompted the evaluation of performing the PEGA polymerizations in solution to see if better control could be attained.

Effect of Monomer-to-Initiator Ratio for Bulk PEGA Polymerizations. The effect of increasing the target molecular weight by adjusting the monomer-to-initiator ratio was also examined to see how kinetic behavior was altered and how $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ were affected. Figure 5 plots $\bar{M}_n$ versus PEGA conversion for target $\bar{M}_n \approx 30$ kg·mol^{-1} and 60 kg·mol^{-1} respectively using $r = 0.21$ at 115 °C in bulk. At the lower target $\bar{M}_n$ of 30 kg·mol^{-1}, the plot was linear up to conversions of about 30% and follows the theoretical line closely in that range.

The experiment targeting the higher $\bar{M}_n$ of 60 kg·mol^{-1} indicated a linear relationship of $\bar{M}_n$ versus conversion up to about 40% conversion but is below the theoretical $\bar{M}_n$ versus conversion plot. Some small, consistent discrepancies may exist between the theoretical prediction and the actual data due to measuring the sample molecular weights relative to linear poly(styrene) standards but this cannot explain how the $\bar{M}_n$ versus conversion plot leveled off at the higher target $\bar{M}_n$. The leveling for the higher monomer-to-initiator ratio was much more noticeable than the data corresponding to the lower monomer-to-initiator ratio. The plateau in the $\bar{M}_n$ versus conversion plot is more likely due to side reactions such as termination which become more prevalent at higher conversion

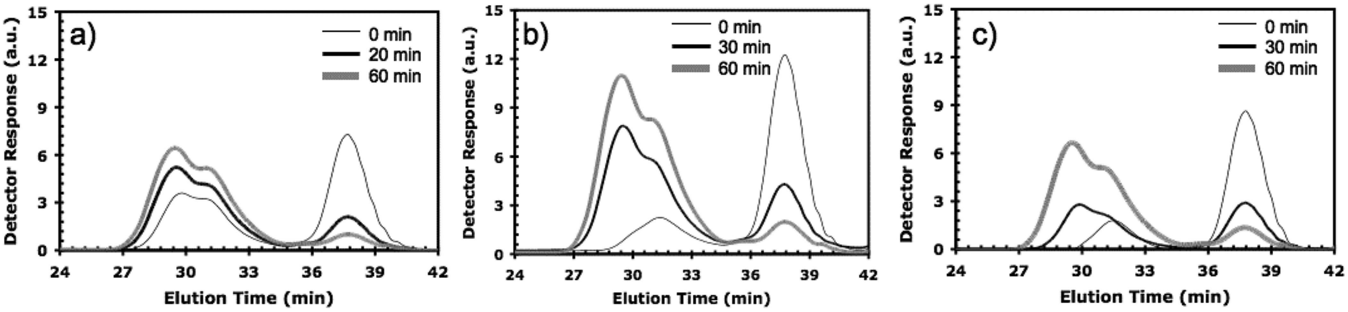


Figure 7. Size exclusion chromatography (SEC) traces for various poly(ethylene glycol) acrylate (PEGA) polymerizations at 115 °C in 50 wt % dimethylformamide (DMF) solution initiated by BlocBuilder and various molar ratios of initially added SG1 free nitroxide relative to BlocBuilder ($r = [\mathrm{SG1}]_0/[\mathrm{BlocBuilder}]_0$). The traces are shown from samples taken at various polymerization times for (a) $r = 0$, (b) $r = 0.05$, and (c) $r = 0.15$.

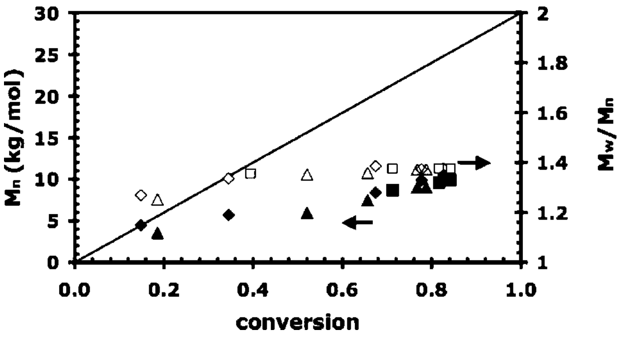


Figure 8. Number average molecular weight (M_n) and polydispersity index (M_w/M_n) versus conversion for various poly(ethylene glycol) acrylate (PEGA) solution polymerizations in dimethylformamide (DMF) performed at 115 °C with various initial molar concentration ratios of SG1 free nitroxide relative to BlocBuilder initiator ($r = [\mathrm{SG1}]_0/[\mathrm{BlocBuilder}]_0$). The M_n of samples taken at various conversions are indicated for $r = 0$ by filled squares (■), for $r = 0.05$ by filled diamonds (◆) and for $r = 0.15$ by filled triangles (▲). The M_w/M_n of samples taken at various conversions are indicated for $r = 0$ by open squares (□), for $r = 0.05$ by open diamonds (◇) and for $r = 0.15$ by open triangles (△).

and chain transfer to polymer by hydrogen abstraction which as noted previously are common in conventional and controlled radical acrylate polymerizations. For higher target $\bar{M}_n$, the probability of at least one lengthy branch becomes more likely, thereby altering the polymer structure and affecting the end group integrity[74] as is suggested by the greater discrepancy between the theoretical $\bar{M}_n$ versus conversion plot for the higher monomer-to-initiator ratio compared to the lower monomer-to-initiator ratio shown in Figure 5.

PEGA Polymerizations in Solution. The previous section indicated that NMP of PEGA in bulk was rapid and a relatively high concentration of free nitroxide was needed to control the polymerization. Polymerizations were thus conducted in DMF or anisole solution at various temperatures and initial SG1 concentrations to determine if less free nitroxide could be used to control the polymerization. Table 5 summarizes the various polymerizations done in solution. In 50 wt % DMF solutions at 115 °C, three different SG1/BlocBuilder ratios were studied ($r = 0$, 0.05, and 0.15) for the polymerization of PEGA. As indicated by the kinetic plot in Figure 6, without any SG1, polymerizations were rapid with some polymer already formed at the initial polymerization time. The rate of polymerization was not very different compared to the bulk polymerizations and the curvature seemed more severe although this was likely due to allowing the polymerization to continue for longer times. Even with more free nitroxide added, the polymerizations were still rapid and the molecular weight distributions became bimodal, indicating a high degree of termination reactions (Figure 7). Further, the $\bar{M}_n$ plateaued relatively early and stayed constant at about 10 $\mathrm{kg \cdot mol^{-1}}$ (relative to poly(styrene) standards) throughout the rest of the polymerization (Figure 8).

We then attempted to slow the polymerization further and gain more control by lowering the polymerization temperature from 115 to 105 °C and decreasing the monomer concentration to 25 wt % in the DMF solution. The polymerization slowed considerably but at conversions ~30%, the bimodality in the molecular weight distribution started to become more prevalent and the $\bar{M}_n$ plateaued. A different solvent was also examined to see if perhaps chain transfer to solvent could be the problem. DMF was initially chosen due to its highly polar nature that makes it a suitable solvent for PEGA. However for other

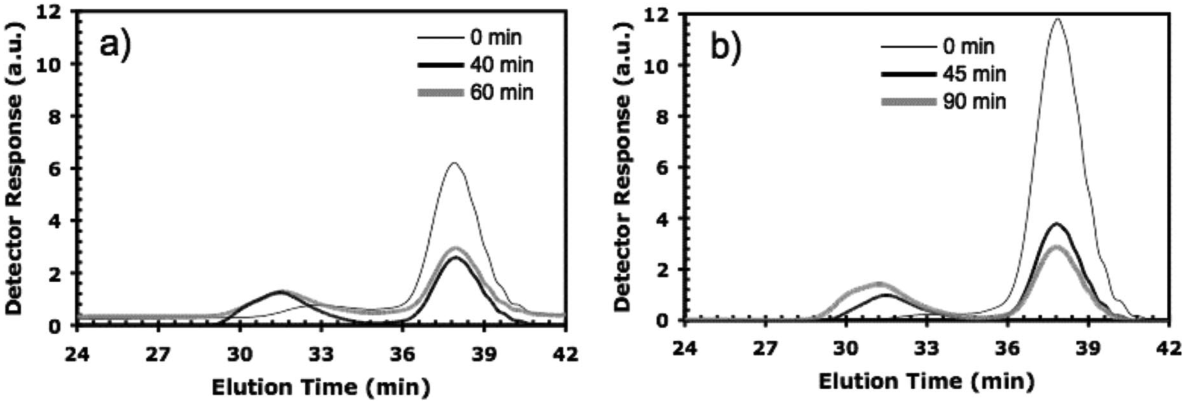


Figure 9. Size exclusion chromatography (SEC) traces for various poly(ethylene glycol) acrylate (PEGA) solution polymerizations taken from various samples at 105 °C in a) 25 wt % dimethylformamide (DMF) solution and b) 25 wt % anisole solution initiated by BlocBuilder. The molar ratio of initially added SG1 free nitroxide relative to BlocBuilder ($r = [\mathrm{SG1}]_0/[\mathrm{BlocBuilder}]_0$) was 0.15 in both cases.

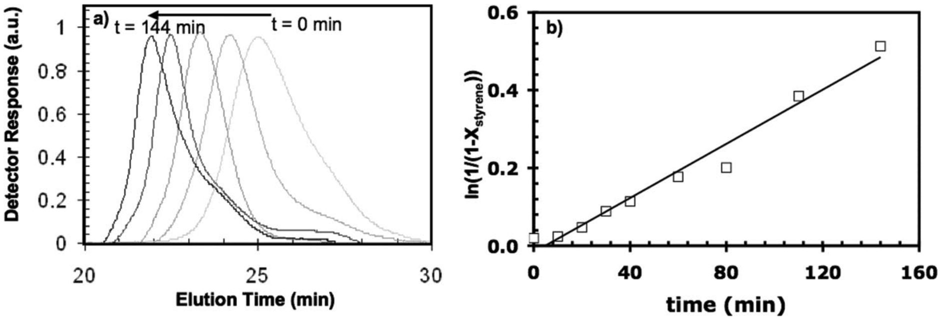


Figure 10. (a) Size exclusion chromatography (SEC) traces taken at various times for the polymerization of styrene at 115 °C in 50 wt % dimethylformamide (DMF) solution initiated from a poly(poly(ethylene glycol) acrylate) (PPEGA) macroinitiator (PPEGA macroinitiator had a number average molecular weight $\bar{M}_n = 8.1$ kg·mol^{-1} and polydispersity index $\bar{M}_w/\bar{M}_n = 1.20$). A small amount of added SG1 free nitroxide relative to the PPEGA macroinitiator was used (ratio of SG1 to that of PPEGA was 0.16). (b) Semilogarithmic plot of scaled conversion ($\ln(1/(1 - X_{styrene}))$) versus polymerization time, where $X_{styrene}$ was the styrene conversion.

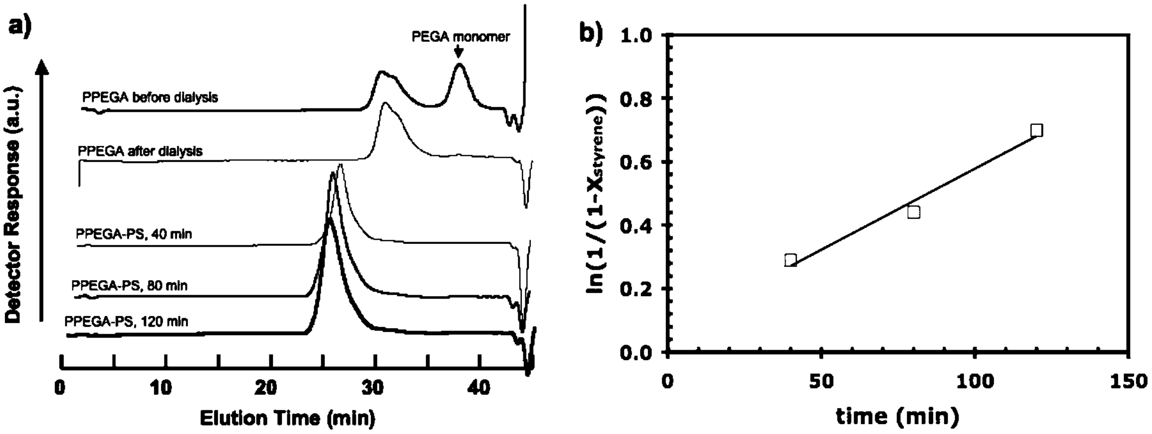


Figure 11. (a) Size exclusion chromatography (SEC) traces taken at various times for the polymerization of styrene at 115 °C in 50 wt % anisole solution initiated from a poly(poly(ethylene glycol) acrylate) (PPEGA) macroinitiator (PPEGA macroinitiator had a number average molecular weight $\bar{M}_n = 8.9$ kg·mol^{-1} and polydispersity index $\bar{M}_w/\bar{M}_n = 1.16$). (b) Semilogarithmic plot of scaled conversion ($\ln(1/(1 - X_{styrene}))$) versus polymerization time, where $X_{styrene}$ was the styrene conversion.

Table 6. Summary of Chain Extension Experiments for Styrene Initiated from Poly(ethylene glycol) Acrylate (PEGA) Macroinitiators in Solution at 115 °C

expt id	macroinitiator (MI) id	$\bar{M}_n$ of MI[a] (kg·mol^{-1})	$\bar{M}_w/\bar{M}_n$ of MI[a]	time (min)	copolymer $\bar{M}_n$ (kg·mol^{-1})[a]	copolymer $\bar{M}_w/\bar{M}_n$[a]
PPEGA−PS-1	PPEGA-5	8.1	1.20	144	62.3	1.53
PPEGA−PS-2	PPEGA-13	8.9	1.16	120	65.6	1.93

[a] Number average molecular weight $\bar{M}_n$ and polydispersity index $\bar{M}_w/\bar{M}_n$ of the poly(poly(ethylene glycol) acrylate) (PPEGA) macroinitiator and the PPEGA-poly(styrene) product was determined by size exclusion chromatography (SEC) using linear poly(styrene) standards in tetrahydrofuran solvent.

monomers, DMF has been found to have relatively high chain transfer constants compared to less polar solvents.[75] We thus chose anisole as an alternative solvent that was used earlier for diethylglycol and triethylene glycol acrylate polymerizations by NMP.[42] The polymerizations slowed considerably as $\bar{M}_w/\bar{M}_n$ was quite low initially and the distribution was monomodal but at higher conversions >30%, the peaks in the SEC chromatograms became increasingly bimodal (Figure 9). From this set of experiments, obviously side reactions in solution are occurring which limit the degree of polymerization. Subsequent decreasing of the polymerization temperature to 95 °C marginally improved the control of the polymerization (Table 5).

One interesting finding from the kinetic analysis was the apparently high concentration of free nitroxide needed to control the polymerization compared to other monomers which is likely due to the nature of the PEGA monomer. A monomer such as styrene typically requires no more than 4.5 mol % free nitroxide SG1 relative to initiator to achieve a high degree of "livingness" with some unimolecular initiators such as MONAMS while no additional free nitroxide is needed for polymerizations employing BlocBuilder. The relatively more hindered BlocBuilder has a higher release rate of SG1 compared to MONAMS and thus does not need additional SG1. *tert*-Butyl acrylate polymerized without any additional SG1 free nitroxide retained a narrow molecular weight distribution and was sufficiently living to initiate the polymerization of styrene to produce poly(*tert*-butyl acrylate)-*b*-poly(styrene) diblock with negligible dead initiating chains.[59,76] Acrylic acid homopolymers[45] and random copolymers with styrene in concentrated solution[57] required higher amounts of added free nitroxide ~9 mol % of free nitroxide to attain a controlled polymerization. The latter case required higher free nitroxide concentrations due to the propensity of the acrylic acid to degrade the SG1 during the polymerization[77] and thus more SG1 was needed to compensate for the SG1 lost to the side reactions. Hydroxyethyl acrylate (HEA) required 6−12 mol % of SG1 free nitroxide initiator to achieve a linear increase in $\bar{M}_n$ with conversions up to 50−60%[47] when MONAMS was used as the unimolecular initiator. In the latter case, more initial free nitroxide was added since the k_p of HEA was expected to be higher compared to other acrylates such as *n*-butyl acrylate[47] and the higher initial free nitroxide concentration was used to effectively prevent excessively high exotherms. We observed some exotherms at lower SG1 initial concentrations in bulk at higher conversions which suggested the PEGA

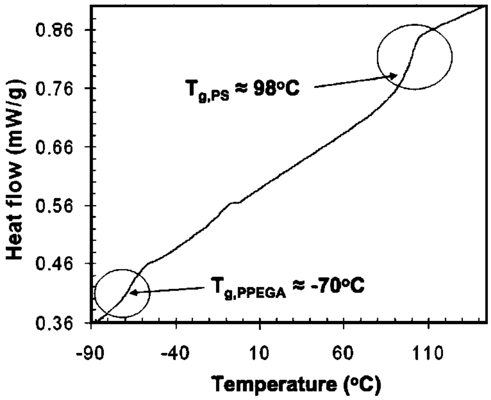


Figure 12. Differential scanning calorimetry (DSC) plot indicating heat flow versus temperature for the poly(ethylene glycol) acrylate-poly(styrene) (PPEGA-*b*-PS) diblock copolymer sample PPEGA−PS-1 (see Table 6 for characterization data). The glass transition temperature of the poly(styrene) segment, $T_{g,PS}$, is seen at about 98 °C while the glass transition temperature of the PPEGA segment, $T_{g,PPEGA}$, is seen at about −70 °C.

k_p is also relatively high. Confirmation of a high k_p could be found by methods such as pulsed laser polymerization (PLP).[78]

Any possible exotherms associated with the bulk PEGA polymerization were limited by performing the polymerizations in solution. However, the effect of chain transfer by hydrogen abstraction has been suggested to be relatively severe for radical polymerizations of PEGA and other related PEG side chain monomers[71,72] and could not be discounted in our solution polymerizations. Additional initial SG1 was used to gain more control and slow the solution polymerizations to prevent any side reactions. Given a sufficient temperature and monomer concentration in solution, the polymerizations were slowed considerably using $r = 0.15$ which suggests that slightly lower SG1 loadings could be used. To determine the effect of chain transfer side reactions more succinctly, the polymerization of oligo(ethylene glycol) methacrylate with the same side chain length as the PEGA examined in this study would be particularly telling as the methacrylate would not be likely as susceptible to hydrogen abstraction as the acrylate. The effect of side reactions of oligo(ethylene glycol) methacrylate was not suggested to be prominent at the conditions reported earlier.[63]

Chain Extension of PPEGA with Styrene. Once the conditions were found to produce PPEGA with a relatively narrow molecular weight and a linear increase in $\bar{M}_n$ versus conversion over a significant conversion range, the chain extension of the block by the addition of a second batch of styrene was attempted in DMF and anisole solutions at 115 °C. For the chain extension in DMF solution, the PPEGA macroinitiator (sample PPEGA-5 shown in Table 1 with $\bar{M}_n = 8.1$ kg/mol, $\bar{M}_w/\bar{M}_n = 1.20$) was able to initiate the polymerization of styrene relatively cleanly as indicated by the SEC chromatograms taken at various times during the polymerization shown in Figure 10a). The chromatograms remained relatively monomodal with negligible homopolymer PPEGA remaining although $\bar{M}_w/\bar{M}_n$ increased up to 1.53 by the end of the polymerization. This particular chain extension was done with some additional SG1 as the same protocol was thought to control a chain extension of acrylic acid better with a poly(styrene) macroinitiator.[79] The conversion of the styrene block determined from samples taken at various polymerization times was measured and shown in Figure 10b) as the scaled conversion plot ($\ln(1 - X_{\text{styrene}})^{-1}$) versus time where X_{styrene} was the conversion of styrene. The conversion of styrene was quite linear in the range studied indicating that the PPEGA chains were substantially capped with active SG1 groups to initiate the second batch of monomer.

A second chain extension in anisole solution was done at 115 °C without using any additional SG1 free nitroxide. In this case addition of the styrene onto the PPEGA macroinitiator (entry PPEGA 13 from Table 5, $\bar{M}_n = 8.9$ kg·mol^{-1}, $\bar{M}_w/\bar{M}_n = 1.16$) was indicated by the clear shift of the peak to higher molecular weights in the SEC traces although again a substantial broadening of the $\bar{M}_w/\bar{M}_n$ to values from 1.70−1.93 was observed (Figure 11a) despite the linear increase in $\ln(1/(1 - X_{\text{styrene}})^{-1})$ with conversion (Figure 11b). Any macroinitiator that failed to initiate the styrene polymerization was not observed in the SEC traces taken after styrene addition. Table 6 summarizes the characterization of the styrene chain extensions from the PPEGA macroinitiators.

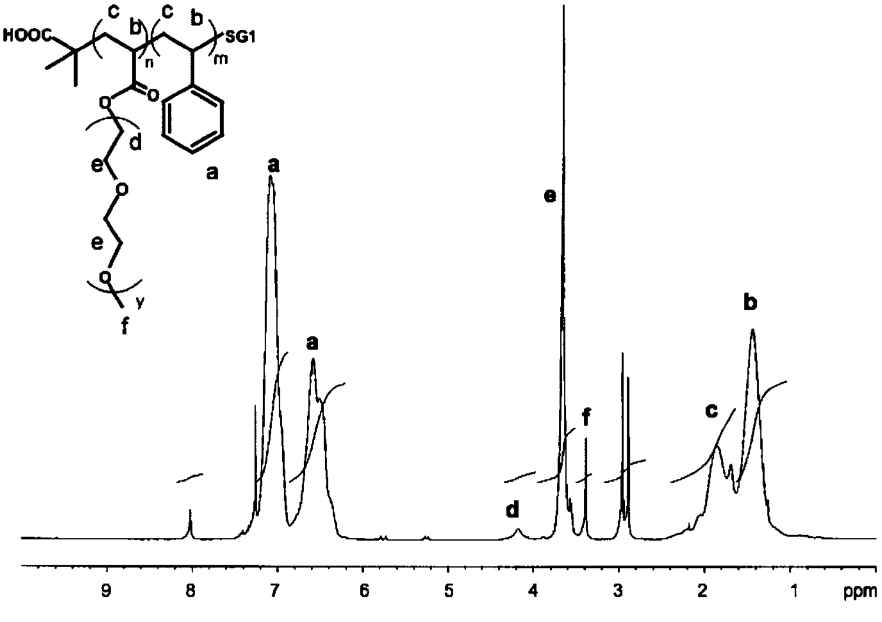


Figure 13. Proton nuclear magnetic resonance (^{1}H NMR) spectrum of poly(ethylene glycol) acrylate-poly(styrene) (PPEGA-*b*-PS) diblock copolymer in $CDCl_3$ corresponding to sample PPEGA−PS-1 (see Table 6 for characterization data).

Characterization of Poly(ethylene glycol) acrylate-*block*-Poly(styrene) (PPEGA-*b*-PS) Diblock Copolymer. To determine if the product polymer had two distinct blocks, differential scanning calorimetry (DSC) was performed. From the DSC trace shown in Figure 12 for sample PPEGA−PS-1, two distinct transitions were observed corresponding to the T_g of PPEGA at approximately −70 °C and that of poly(styrene) (PS) at 98 °C along with a small peak due likely to melting of the PEG units at approximately 0 °C. Similar transitions were observed for random copolymers consisting of acrylate or methacrylate monomers having longer PEG side-chains ($\bar{M}_n \sim 2$ kg/mol) with styrene[80] and methylmethacrylate[81] in addition to comb-like PEG acrylate and methacrylate-based polymers.[82−84] The T_g corresponding to the PEG block is lower than the literature value of −50 °C[75] since the side chain of the PEGA used in this study was very short with only 8 EG repeat units. The short PEG side chains are also likely to have depressed the melting temperature T_m of the PEG segment (compared to the literature value of 66 °C)[75] while also not being as crystalline as longer PEG segments would be expected to be.

The compositions of the PPEGA−PS block copolymers were determined using ^{1}H NMR spectroscopy and the spectrum for the copolymer sample PPEGA−PS-1 (Table 6) is shown in Figure 13. Given that the PS segment has a signal corresponding to 5 aromatic protons at 6.6−7.1 ppm and the PEG side chain from the PPEGA segment has 4 protons per EG unit at 3.7 ppm, the composition of the block copolymer can be determined. For the analysis, the comparison was done between the 5 protons from the aromatic ring found at 6.6−7.1 ppm (corresponding to an integration of 45.04 units) and the 4 protons on the PEG side chain that appear at 3.7 ppm (corresponding to an integration of 10.64 units). Equations 4−6 show the appropriate calculations that lead to the determination of the mole fraction of EG in the copolymer to be 23 mol %. In terms of PEGA, since there are 8 EG units per chain in the monomer, the mol fraction of PEGA was calculated to be 3.7 mol % in the copolymer.

$$\frac{I_{-\mathrm{CH_2CH_2O}-}}{\text{no. of protons}} = \text{moles of EG units} \tag{4}$$

$$\frac{I_{-\mathrm{C_6H_5}-}}{\text{no. of protons}} = \text{moles of styrene units} \tag{5}$$

$$f_{EG} = \frac{\text{moles of EG units}}{\text{moles of EG units} + \text{moles of styrene units}} = \frac{(10.64/4)}{(10.64/4) + (45.04/5)} = 0.23 \tag{6}$$

Conclusions

Kinetic parameters were determined for the controlled bulk polymerization of poly(ethylene glycol) acrylate (PEGA) using BlocBuilder unimolecular initiator and additional SG1 free nitroxide. Low $\bar{M}_w/\bar{M}_n$ (<1.3) and linear increases in $\bar{M}_n$ versus conversion were favored using a lower temperature of 115 °C and initial molar ratio of free SG1 nitroxide with respect to BlocBuilder (r) > 0.10. Very little difference in control was observed when r was increased to up to 0.21. The k_pK value at 115 °C found for PPEGA varied between 1.9×10^{-5} s^{-1} to 2.9×10^{-5} s^{-1} which was comparable to other acrylates such as n-butyl acrylate, acrylic acid and hydroxyethyl acrylate. At 125 °C, k_pK values for PPEGA were estimated to be from 6.7×10^{-5} s^{-1} to 8.3×10^{-5} s^{-1} although these values are subject to error as the polymerizations were not particularly controlled at 125 °C and low r. "Livingness" of the PPEGA chain end was confirmed by chain extension of PPEGA ($\bar{M}_n \sim 8$ kg/mol, $\bar{M}_w/\bar{M}_n \sim 1.20$) with styrene in DMF and anisole solution at 115 °C as the SEC chromatograms indicated that the samples remained monomodal and relatively monodisperse as the polymerization proceeded although the molecular weight distributions of the resulting block copolymers broadened considerably with $\bar{M}_w/\bar{M}_n = 1.53-1.93$. Incorporation of the PS and PPEGA segments into the diblock was indicated by two distinct T_g's corresponding to the PPEGA and PS segments and by the distinct resonances observed by ^{1}H NMR spectroscopy. Examination of the block copolymer morphology and surface properties is now in progress.

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