

# Nitroxide-Mediated Synthesis of Styrenic-Based Segmented and Tapered Block Copolymers Using Poly(lactide)-Functionalized TEMPO Macromediators

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**ABSTRACT:** Poly(styrene)-poly(lactide) (PS-PLA), poly(*tert*-butyl styrene)-poly(lactide) (*Pt*BuS-PLA) diblocks, and poly(*tert*-butyl styrene)-poly(styrene)-poly(lactide) (*Pt*BuS-PS-PLA) segmented and tapered triblocks of controlled segment lengths were synthesized using nitroxide-mediated controlled radical polymerization. Well-defined PLA-functionalized macromediators derived from hydroxyl terminated TEMPO (PLA<sub>T</sub>) of various molecular weights mediated polymerizations of the styrenic monomers in bulk and in dimethylformamide (DMF) solution at 120–130°C. PS-PLA and *Pt*BuS-PLA diblocks were characterized by narrow molecular weight distributions (polydispersity index ( $M_w/M_n$ ) < 1.3) when using the PLA<sub>T</sub> mediator with the lowest number average molecular weight  $M_n = 6.1$  kg/mol while broader molecular weight distributions were exhibited ( $M_w/M_n = 1.47$ – $1.65$ )

when using higher molecular weight mediators ( $M_n = 7.4$  kg/mol and 11.3 kg/mol). Segmented *Pt*BuS-PS-PLA triblocks were initiated cleanly from *Pt*BuS-PLA diblocks although polymerizations were very rapid with PS segments ~ 5–10 kg/mol added within 3–10 min of polymerization at 130°C in 50 wt % DMF solution. Tapering from the *Pt*BuS to the PS segment in semibatch mode at a lower temperature of 120°C and in 50 wt % DMF solution was effective in incorporating a short random segment of *Pt*BuS-*ran*-PS while maintaining a relatively narrow monomodal molecular weight distribution ( $M_w/M_n \approx 1.5$ ). © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 3185–3195, 2008

**Key words:** block copolymers; polystyrene; ring-opening polymerization; radical polymerization; templates

## INTRODUCTION

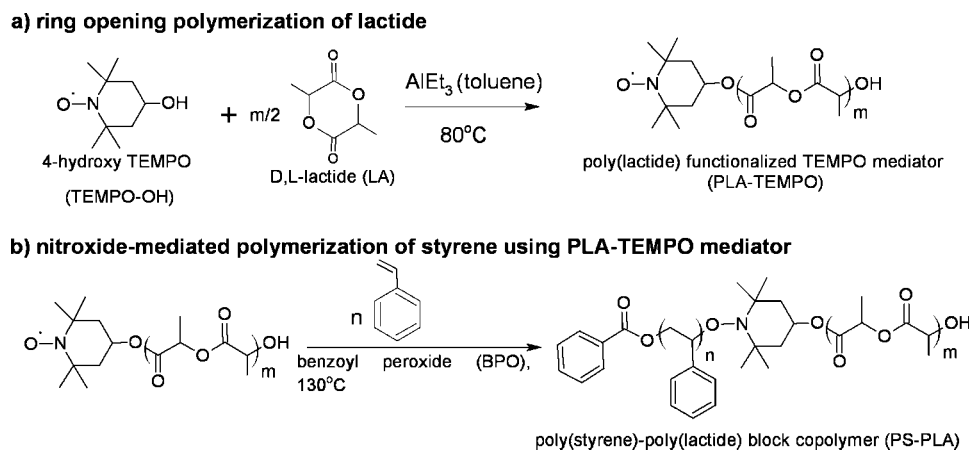
The striking ability of AB and ABC triblock copolymers with precisely controlled segment lengths to self-assemble at the nanometer scale has enormous utility for applications ranging from thermoplastic elastomers,<sup>1</sup> catalyst supports,<sup>2</sup> organic photovoltaics,<sup>2,3</sup> and nanoporous media.<sup>4–12</sup> Traditionally, such block copolymers could only have been produced by methods such as “living” ionic polymerization which require strict control of reagent purity and air-free environments. The development of controlled radical polymerization methods such as reversible addition fragmentation transfer (RAFT) polymerization,<sup>13</sup> atom transfer radical polymerization (ATRP),<sup>14</sup> and nitroxide-mediated polymerization (NMP)<sup>15,16</sup> provide nearly the same control of microstructure as traditional ionic polymerization methods without the extensive purification of reagents required. Further,

monomer sequences that cannot be made by ionic polymerization can be directly accessed using controlled radical polymerization.<sup>17</sup> In some cases, ionic polymerization methods have been combined with controlled radical polymerization methods to produce unique functional materials. For example, Rzayev and Hillmyer described the synthesis of ABC triblocks where poly(dimethylacrylamide) (PDMA) segments were produced using RAFT which used a chain transfer agent functionalized with a poly(lactide) (PLA) produced previously by ring-opening polymerization.<sup>10</sup>

Despite the utility of controlled radical polymerization to produce such structurally tailored segmented copolymers, ABC segmented blocks may however be difficult to implement industrially as a sequential process. A semibatch method may be favorable to avoid an intermediate purification step. We evaluated such a protocol by comparing the synthesis of segmented blocks using a PLA functionalized macromediator derived from 4-hydroxy-2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO-OH) as shown in Figure 1. After catalyzing ring-opening polymerization of D,L-lactide from TEMPO-OH using a metallic initiating species, the resulting PLA-TEMPO species was used to control polymerizations of sty-

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**Figure 1** Scheme to produce styrenic-based block copolymers with poly(lactide) (PLA) via ring-opening polymerization and subsequent nitroxide mediated polymerization. First, the hydroxyl functional TEMPO is used as an initiator for the ring-opening polymerization of lactide to produce the poly(lactide) functionalized TEMPO mediator (PLA<sub>T</sub>) shown in (a). The PLA<sub>T</sub> mediator is then used to polymerize styrene or *tert*-butyl styrene with a conventional initiator such as benzoyl peroxide (BPO) to make the desired styrenic-based block copolymer (b).

rene and *tert*-butyl styrene (*t*BuS). The polymerization of *tert*-BuS using a PLA functionalized macro-mediator followed by addition of styrene to produce a segment consisting of *Pt*BuS which gradually tapers into a segment of PS to produce the *P(t*BuS-*tap*-S)-PLA copolymer was then compared to the segmented approach. The styrene containing segment in such block copolymers can then be selectively modified to introduce functional groups for many desired applications.<sup>18–25</sup>

## EXPERIMENTAL SECTION

### Materials

Styrene (99%), 4-*tert*-butyl styrene (93%), basic alumina (150 mesh), calcium hydride (90% reagent grade), benzoyl peroxide (BPO) (97% reagent grade), 4-hydroxy-TEMPO (97%), and triethyl aluminum (1.8M in toluene) were acquired from Sigma-Aldrich (Oakville, ON, Canada). *N,N*-dimethyl formamide (99.8%) was purchased from Fisher Scientific (Montreal, QC, Canada), D,L-lactide (LA) was purchased from Polysciences (Warrington, PA), and ethyl acetate (99.5%) was obtained from EMD Chemicals (Gibbstown, NJ). Tetrahydrofuran (THF) (99%) and phenylhydrazine (97%) were acquired from Caledon Laboratories (Georgetown, ON, Canada). 4-*tert*-butyl styrene and styrene monomers were purified in a 250 mL fritted glass column packed with 45 g of basic alumina oxide and 5 g of calcium hydride to remove the inhibitor and any other protic impurities. Dimethyl formamide (DMF) was purified similarly. Purified monomer was collected directly from the column in a sealed flask, stored under nitrogen and kept in a refrigerator until needed. LA was purified

by recrystallization from ethyl acetate solution. All other reagents were used as received.

### Macromediator synthesis

Poly(lactide) functionalized TEMPO (PLA-TEMPO) macromediators were produced from the ring-opening polymerization of LA in a similar manner performed earlier for poly(tetrahydrofuran),<sup>26</sup> poly(ε-caprolactone),<sup>27,28</sup> and poly(ethylene adipate)<sup>29</sup> functionalized TEMPO. Macromediator synthesis was performed in toluene at 80°C using 4-hydroxy TEMPO (TEMPO-OH) as the initiator for the ring-opening polymerization of LA catalyzed by triethyl aluminum (AlEt<sub>3</sub>). A sample synthesis is described as follows for a PLA-TEMPO macromediator with a desired molecular weight of 10 kg/mol (entry PLA<sub>T</sub>-10 in Table I). TEMPO-OH (0.34 g, 2 mmol) and LA (10 g, 0.069 mol) were added to two separate flasks that had been previously silanized (a 250 mL Air Free Schlenk and Aldrich Sure/Stor<sup>TM</sup> flask, respectively). To the flask containing the TEMPO-OH, a Teflon coated stir bar was added and a rubber septum was used to seal the neck. The flask was connected to an 8907A Welch high vacuum pump to remove any volatile impurities. After pumping out the reactor for 12 h at room temperature, the reactor was purged with nitrogen and 20 mL of dry toluene previously purified through a column of basic alumina was added by cannula. The flask containing LA was dried in a vacuum oven for a period of 24 h at 40°C, sealed and then to it was added 80 mL of dry toluene by cannula. After 1 h, 0.28 mL AlEt<sub>3</sub> solution in hexane (~1.8M) was slowly added to the reactor. The reactor was connected to a bubbler to monitor any pressure changes and observe the

**TABLE I**  
**Poly(lactide)-TEMPO (PLA<sub>T</sub>) Macromediator**  
**Characterization**

	$M_{n,NMR}^a$ (kg/mol)	$M_n^b$ (kg/mol)	$M_w^b$ (kg/mol)	$M_w/M_n^b$
PLA <sub>T</sub> -4	5.4	6.1	7.7	1.26
PLA <sub>T</sub> -6	— <sup>a</sup>	7.7	9.2	1.24
PLA <sub>T</sub> -10	10.5	11.3	13.2	1.19

<sup>a</sup> Number average molecular weight  $M_n$  determined by <sup>1</sup>H NMR in CDCl<sub>3</sub> with phenylhydrazine for the highest and lowest target molecular weight macromediators.  $M_n$  of PLA<sub>T</sub>-6 was not measured by <sup>1</sup>H NMR since it was consumed in other experiments.

<sup>b</sup> Molecular weights determined using gel permeation chromatography (GPC) in tetrahydrofuran (THF) at 40°C relative to poly(styrene) standards.

release of the ethane byproduct caused by the formation of alkoxide initiator. The solution was then allowed to stir for a period of 2 h to allow for the formation of the aluminum alkoxide macroinitiator.

Once the macroinitiator was formed, the LA previously dissolved in toluene at ~ 80°C was added by cannula. The reactor was then submerged in an oil bath set at 90°C for a period of 60 h to start the polymerization. The reaction was terminated by adding 10 mL of acidic methanol. The reactor was removed from the oil bath and cooled to room temperature. A rotary evaporator was then used to concentrate the solution and the contents were then poured into a beaker containing (200 mL) of hexane to precipitate the polymer. The orange-colored polymeric product immediately settled to the bottom of the beaker. The top layer of liquid was then decanted and the rest was filtered under vacuum and dried in a vacuum oven for 24 h at 60°C. The orange-yellow solids were recovered (6.8 g, yield = 68%) with number average molecular weight  $M_n = 11.3$  kg/mol, weight average molecular weight  $M_w = 13.2$  kg/mol, and polydispersity index  $M_w/M_n = 1.19$  as measured by gel permeation chromatography (GPC) relative to poly(styrene) standards in THF at 40°C. The  $M_n$  determined by <sup>1</sup>H-NMR was 10.4 kg/mol. The target molecular weight for other PLA-TEMPO mediators was varied by altering the ratio of TEMPO-OH to LA. Table I summarizes the molecular weight characteristics for the three PLA-TEMPO macromediators that were subsequently used for nitroxide-mediated styrenic polymerizations.

### Segmented diblock copolymer synthesis

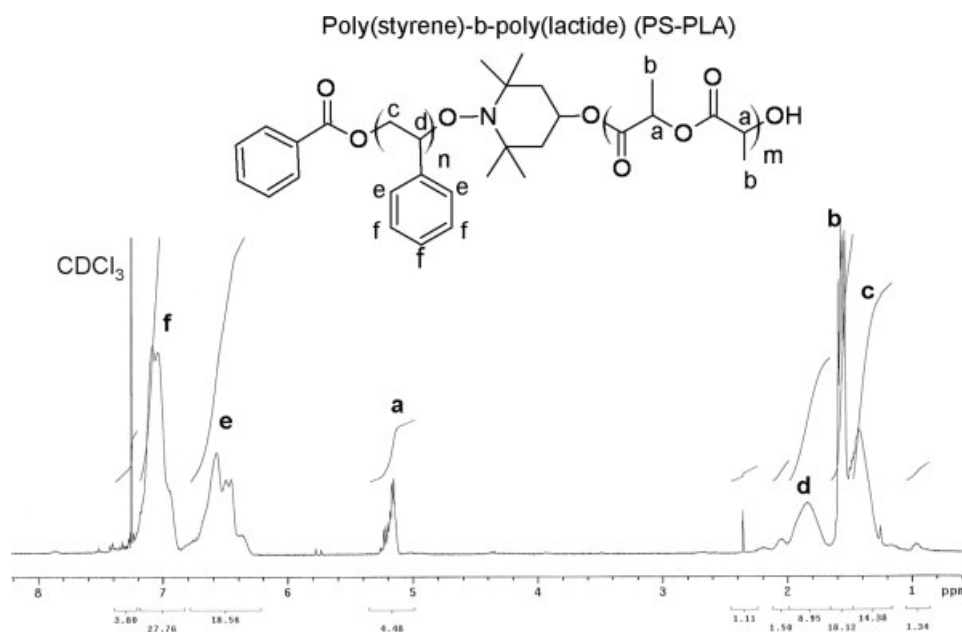
All reactions were carried out in a two-neck 100 mL reactor equipped with a thermal well and a teflon-coated magnetic stir bar. A sample synthesis is provided using PLA<sub>T</sub>-4 macromediator and styrene

monomer polymerized in bulk. PLA<sub>T</sub>-4 macromediator (2.0 g, 0.33 mmol,  $M_n = 6.1$  kg/mol,  $M_w/M_n = 1.26$ ) and the benzoyl peroxide (BPO) initiator (0.07 g, 0.29 mmol) were added to the reactor. In all cases, the molar ratio of macromediator to BPO was kept to nearly 1 : 1. Table II lists all the formulations used to produce the various blocks in bulk and in dimethyl formamide (DMF) solution. One reactor port was sealed using a rubber stopper. A cooling condenser was inserted into the other port, and a thermocouple attached to a controller was inserted into the thermal well. A glycol/water mixture was used to cool the condenser via a recirculating bath (Neslab RTE-7) set at 0°C. Previously purified styrene (5.1 g, 0.049 mol) was cannulated from its sealed flask into the sealed reactor using nitrogen pressure. The reactor was placed in a heating mantle and was then

**TABLE II**  
**Polymerization Formulations for Styrenic**  
**Polymerizations Mediated by Various Poly(lactide)**  
**Functionalized TEMPO Mediators (PLA<sub>T</sub>)**

	Poly(lactide) macromediator <sup>a</sup>		
	PLA <sub>T</sub> -4	PLA <sub>T</sub> -6	PLA <sub>T</sub> -10
PS-PLA <sub>T</sub> diblocks			
PS block target $M_n$ (kg/mol)	10	14	20
Styrene (g)	5.0	5.0	5.0
PLA <sub>T</sub> (g)	2.0	2.1	2.5
Benzoyl peroxide (BPO) (g)	0.07	0.04	0.03
Temperature (°C)	130	130	130
PS-PLA <sub>T</sub> diblocks for kinetic analysis			
PS block target $M_n$ (kg/mol)	61	—	112
Styrene (g)	15.3	—	15.0
PLA <sub>T</sub> (g)	1.5	—	1.5
Benzoyl peroxide (BPO) (g)	0.060	—	0.033
Temperature (°C)	125	—	125
PtBuS-PLA <sub>T</sub> diblocks			
PtBuS block target $M_n$ (kg/mol)	10	14	20
<i>Tert</i> -butyl styrene (g)	5.0	5.0	5.0
PLA <sub>T</sub> (g)	1.0	1.5	1.0
Benzoyl peroxide (BPO) (g)	0.03	0.03	0.012
Dimethylformamide (DMF) (g)	—	5.0	5.0
Temperature (°C)	130	130	130
PtBuS-PS-PLA <sub>T</sub> (segmented blocks)			
Styrene (g)	12.0	5.1	6.0
PtBuS-PLA <sub>T</sub> (g)	0.65	0.5	0.5
Benzoyl peroxide (BPO) (g)	0.010	0.002	0.002
Dimethylformamide (DMF) (g)	—	4.9	6.8
Temperature (°C)	120	120	120
PtBuS-P( <i>t</i> BuS- <i>r</i> -S)-PLA <sub>T</sub> (tapered blocks)			
<i>Tert</i> -butyl styrene (g)	—	10.0	10.9
Styrene (g)	—	8.0	8.1
PLA <sub>T</sub> (g)	—	3.0	2.0
Benzoyl peroxide (BPO) (g)	—	0.061	0.061
Dimethylformamide (DMF) (g)	—	10.0	10.8
Temperature (°C)	—	120	120

<sup>a</sup> Poly(lactide) functionalized TEMPO mediator (PLA<sub>T</sub>) molecular properties are summarized in Table I.



**Figure 2**  $^1\text{H}$  nuclear magnetic resonance (NMR) spectrum in  $\text{CDCl}_3$  of a poly(styrene)-poly(lactide) diblock (PS-PLA) that was derived from the nitroxide-mediated bulk polymerization of styrene at  $130^\circ\text{C}$  mediated by a PLA functionalized TEMPO mediator (PLA<sub>T</sub>-4 with number average molecular weight  $M_n = 6.1$  kg/mol, weight average molecular weight  $M_w = 7.7$  kg/mol, polydispersity index  $M_w/M_n = 1.26$ ). The block copolymer shown here is summarized in Table III as entry PS-PLA<sub>T</sub>-4 ( $M_n = 11.6$  kg/mol,  $M_w = 14.9$  kg/mol,  $M_w/M_n = 1.29$ ). The volume fraction of lactide in the block copolymer determined from the integration of the  $^1\text{H}$  peaks in the NMR spectrum was 22%.

purged for 10 min using nitrogen before the temperature was increased to  $130^\circ\text{C}$ . After the set-point temperature was reached,  $\sim 0.1$  mL samples were taken at regular intervals using a syringe and stored in 4 mL vials containing excess methanol to precipitate the polymeric product. Heating was stopped when the reaction mixture became too viscous to remove any further samples. In this particular case, the reaction was stopped after 193 min. The reactor was cooled to  $40^\circ\text{C}$ , and 40 mL of THF were added to dissolve the reaction mixture and facilitate removal from the reactor. The contents of the reactor were then emptied into 350 mL of methanol to precipitate the polymer. The polymer was recovered using vacuum filtration, and dried in a vacuum oven at  $50^\circ\text{C}$  along with the samples taken during the experiment. The dry samples and final product were weighed to obtain conversion data. For the specific example, 5.92 g of polymeric product was recovered corresponding to a yield of 83%. The final block copolymer molecular weight was  $M_n = 11.6$  kg/mol,  $M_w = 14.9$  kg/mol,  $M_w/M_n = 1.29$  according to GPC relative to poly(styrene) standards in THF at  $40^\circ\text{C}$  while the composition of the block copolymer as determined by  $^1\text{H}$  nuclear magnetic resonance (NMR) in deuterated chloroform ( $\text{CDCl}_3$ ) was 22% by volume PLA using the resonance at a chemical shift  $\delta = 5.1$  ppm as a marker for lactide and the aromatic protons at  $\delta = 6.5\text{--}7.1$  ppm as a marker for

the concentration of styrene in the polymer. The volume fractions of PLA in the block copolymer were converted from the molar fractions from the NMR data using literature values for the room temperature densities  $\rho$  of PLA ( $\rho_{\text{PLA}} = 1.248$  g/cm $^3$ ) and PS ( $\rho_{\text{PS}} = 1.02$  g/cm $^3$ ). $^{30}$  The resonances due to poly(styrene) are given as follows:  $\delta = 1.4\text{--}1.7$  ppm (multiplet,  $-\text{CH}-(\text{C}_6\text{H}_5)-\text{CH}_2-$ );  $\delta = 6.5$  ppm (2H from aromatic group) and  $\delta = 7.1$  ppm (3H from aromatic group). The resonances due to PLA are as follows:  $\delta = 1.6$  ppm (multiplet,  $-\text{C}(\text{O})-\text{CH}(\text{CH}_3)-\text{O}-$ ) and  $\delta = 5.1$  ppm (multiplet,  $-\text{C}(\text{O})-\text{CH}(\text{CH}_3)-\text{O}-$ ). The  $^1\text{H}$ -NMR spectrum in  $\text{CDCl}_3$  for the diblock copolymer PS-PLA<sub>T</sub>-4 is shown in Figure 2. For the poly(*tert*-butyl styrene)-poly(lactide) blocks (PtBuS-PLA), the resonances are identical to those of the PS-PLA blocks except that the protons from the *tert*-butyl group ( $-\text{CH}_2-\text{CH}-\text{C}_6\text{H}_4-\text{C}(\text{CH}_3)_3-$ ) are found at  $\delta = 1.3$  ppm. Polymerizations using DMF as the solvent were performed similarly to those in bulk with DMF being cannulated into the reactor after the transfer of the monomer so that the concentration of the monomer was 50% by mass.

### Segmented triblock copolymer synthesis

A sample synthesis of a poly(*tert*-butylstyrene)-poly(styrene)-poly(lactide) (PtBuS-PS-PLA) segmented

block copolymer using the poly(lactide) functionalized TEMPO mediator PLA<sub>T</sub>-6 described in Table I is given. Using the same reactor set-up for the PS-PLA and PtBuS-PLA diblock syntheses, 0.5 g of PtBuS-PLA<sub>T</sub>-6 (0.032 mmol,  $M_n = 15.8$  kg/mol,  $M_w = 26.2$  kg/mol,  $M_w/M_n = 1.65$ ) was added along with 6.0 g of styrene (0.058 mol), 6.8 g of DMF, and 0.002 g of BPO (0.008 mmol) and sealed inside the reactor. After sparging with ultra-pure nitrogen for 15 min, the reactor was heated to 120°C. After 3 min at 120°C, the polymerization was stopped by shutting off the heating to the reactor. The reactor contents were poured into excess methanol to precipitate the block copolymer which was subsequently recovered by vacuum filtration. The wet cake was then placed inside a vacuum oven at 60°C for 24 h to remove residual solvent and monomer. The resulting product yield was 4.8 g (74%) and the block copolymer was characterized by GPC for molecular weight determination relative to poly(styrene) standards in THF ( $M_n = 28.5$  kg/mol,  $M_w = 48.1$  kg/mol,  $M_w/M_n = 1.69$ ). The composition of styrene relative to *tert*-butyl styrene for the specific example cited was 39 mol % based on <sup>1</sup>H-NMR in CDCl<sub>3</sub>. The relative compositions of the styrenic blocks was determined by examining the ratios of aromatic protons expected for styrene (3 : 2 for chemical shifts  $\delta$  observed at 7.1 and 6.5 ppm, respectively) to that expected for *t*-butyl styrene (2 : 2 for  $\delta = 7.1$  and 6.5 ppm, respectively). The volume fraction of PLA in the block copolymer was 10% using the signal at  $\delta = 5.1$  ppm as a marker for PLA in comparison the aromatic protons of the styrenic units.

### Tapered block copolymer synthesis

A sample synthesis of a poly(*tert*-butylstyrene)-*tap*-poly(styrene)-poly(lactide) tapered block copolymer is given. The same reactor as described above for the synthesis of the diblock copolymers was used to make the tapered blocks. For example, 2.0 g (0.18 mmol) of PLA<sub>T</sub>-10 macromediator ( $M_n = 11.3$  kg/mol,  $M_w = 13.2$  kg/mol,  $M_w/M_n = 1.19$ ) was added to the reactor along with 0.061 g (0.25 mmol) of BPO initiator with 10.8 g of DMF, and 10.9 g of previously purified *tert*-butyl styrene. The reactor was sealed and after purging for 15 min with ultra-pure nitrogen, heating of the reactor to 120°C was started. The initial time of the reaction was taken when the set-point reached 120°C. Aliquots were taken at intervals of approximately 5 min for determination of molecular weight by extraction with a syringe and quenching in methanol. The solution became very viscous after 12 min polymerization after which 8.1 g of styrene was added. The reaction continued for another 26 min and the polymerization was stopped after 38 min. Once the reactor contents had

sufficiently cooled, the reactor contents were poured into excess methanol to precipitate the polymer. The resulting yield was 6.7 g corresponding to a yield of about 52%. The tapered block copolymer molecular weight characteristics were  $M_n = 16.8$  kg/mol,  $M_w = 25.5$  kg/mol,  $M_w/M_n = 1.52$  according to GPC relative to poly(styrene) standards in THF. <sup>1</sup>H-NMR revealed the tapered segment consisted of 13 mol % styrene relative to *tert*-butyl styrene while the lactide volume fraction in the block copolymer was 14%.

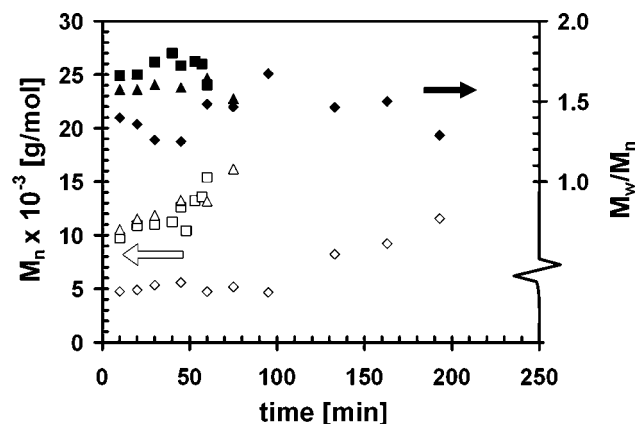
### Characterization

The molecular weight distribution of each sample was characterized using GPC (Waters Breeze) with THF being used as the mobile phase. The mobile phase flow rate was set to 0.3 mL min<sup>-1</sup>. The GPC was equipped with 3 Styragel<sup>®</sup> HR columns (HR1 with molecular weight measurement range of 10<sup>2</sup> to 5 × 10<sup>3</sup> g/mol, HR2 with molecular weight measurement range of 5 × 10<sup>2</sup> to 2 × 10<sup>4</sup> g/mol and HR4 with molecular weight measurement range 5 × 10<sup>3</sup> to 6 × 10<sup>5</sup> g/mol) and a guard column. During the molecular weight analysis, the columns were heated to 40°C. The GPC was initially calibrated using narrow molecular weight distribution poly(styrene) standards, and the molecular weights of the samples were reported relative to the poly(styrene) standards. The GPC was equipped with ultraviolet (UV 2487) and differential refractive index (RI 2410) detectors. The UV detector wavelength was set to 255 nm to detect the aromatic rings in the styrenic-based polymers. <sup>1</sup>H-NMR was performed using a 200 MHz Varian Gemini 2000 spectrometer. Ten milligrams of sample were dissolved in 0.7 mL of deuterated chloroform (CDCl<sub>3</sub>) (Cambridge Isotope Laboratories, Andover, MD) in 5 mm 508 Up NMR tubes. The samples were injected into the probe, shimmed, and scanned 32 times. For the determination of  $M_n$  for the macromediators, 128 scans were performed with addition of phenylhydrazine. Polymer yields were determined gravimetrically by drying under vacuum typically for 24 h at about 60°C or until constant weight was achieved.

## RESULTS AND DISCUSSION

### Synthesis of poly(lactide)-TEMPO (PLA-TEMPO) macromediators

The characterization of the PLA-TEMPO macromediators derived from the ring-opening polymerization of lactide initiated from the hydroxyl-terminated TEMPO is summarized in Table I. The three macromediators had  $M_w/M_n$  in the range of 1.19–1.26 which may be considered relatively large compared to related lactide ring-opening polymerizations

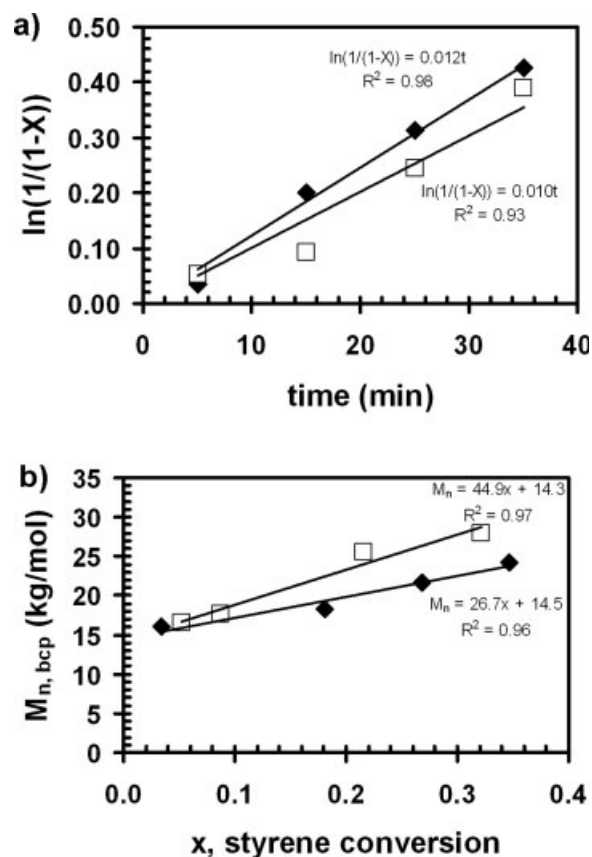


**Figure 3** Number average molecular weight ( $M_n$ ) versus time for the polymerization of styrene at 130°C using poly(lactide)-TEMPO (PLA<sub>T</sub>) macromediators in bulk. Open symbols represent  $M_n$  versus time ( $t$ ) data ( $\diamond$  = PLA<sub>T-4</sub>,  $\square$  = PLA<sub>T-6</sub>,  $\triangle$  = PLA<sub>T-10</sub>) and filled symbols represent polydispersity index (defined as the ratio of weight average to number average molecular weight =  $M_w/M_n$ ) versus time data for each series controlled by the macromediators. The molecular characteristics of the PLA<sub>T</sub> macromediators are summarized in Table I and the characteristics of the PS-PLA<sub>T</sub> block copolymers are summarized in Table III.

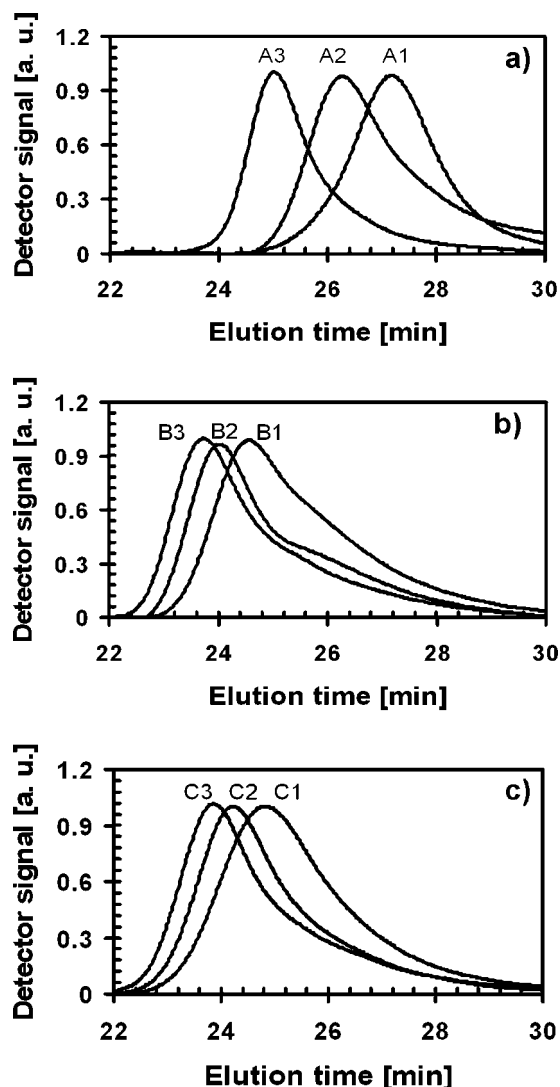
which frequently attain  $M_w/M_n < 1.1$ . This is likely due to the methods used to purify the reagents and the equipment used for polymerization. Solvent was purified using column purification with basic alumina instead of more rigorous distillation procedures. Glove boxes and vacuum manifolds typically used for transfer of reagents were not available and thus simplified transfers via cannulae and Schlenk flasks were used. We expected the molecular weight distributions would broaden slightly with our simplified procedures compared to more rigorous literature procedures and we are aware that increasing polydispersity in the PLA minor phase can increase domain spacing, alter the copolymer morphology to one with increasing mean curvature and decrease the segregation strength at the order-disorder transition.<sup>31,32</sup> For example, Lynd and Hillmyer<sup>31,32</sup> reported the segregation strength at the order-disorder transition temperature  $(\chi N)_{ODT}$  (where  $\chi$  is the enthalpic interaction parameter and  $N$  is the total number of repeat units in the block copolymer) decreased by about 10% when the  $M_w/M_n$  of the PLA segment increased from 1.18 to 2.05 for PLA-poly(ethylene-*alt*-propylene) diblocks. Our moderate increase in polydispersity will likely not greatly affect the ordering of our blocks although we intend to test this by stopping ring-opening polymerizations of lactide at lower conversions which would presumably limit termination or reshuffling reactions that broaden the molecular weight distribution.

### Nitroxide-mediated polymerization of styrene using poly(lactide)-TEMPO (PLA-TEMPO) macromediators

Kinetic data collected from the polymerization of styrene using the various PLA-TEMPO macromediators are presented in Figures 3 and 4. In Figure 3, the target number average molecular weight ( $M_{n,target}$ ) of the poly(styrene) (PS) block using the PLA<sub>T-4</sub>, PLA<sub>T-6</sub> and PLA<sub>T-10</sub> macromediators was 10, 14, and 20 kg/mol, respectively. In Figure 4,  $M_{n,target}$  for the PS block was 61 and 112 kg/mol for the PLA<sub>T-4</sub> and PLA<sub>T-10</sub>, respectively. When conducted in bulk with the lower target molecular weights, the reaction mixture rapidly became very viscous and samples were difficult to remove, resulting in polymerizations being stopped after approximately 2–3 h. Only the polymerization using the 4 kg/mol macromediator resulted in a narrow molecu-



**Figure 4** (a) Semilogarithmic plot of  $\ln(1/(1-X))$  ( $X$  = styrene conversion) versus time for styrene polymerizations mediated by PLA<sub>T-4</sub> (indicated by filled diamonds  $\blacklozenge$ ) and PLA<sub>T-10</sub> (indicated by open squares  $\square$ ) macromediators in bulk at 125°C. (b) Number average molecular weight of block copolymer ( $M_{n,bcp}$ ) according to poly(styrene) standards by GPC versus conversion of styrene for the polymerizations using PLA<sub>T-4</sub> (indicated by filled diamonds  $\blacklozenge$ ) and PLA<sub>T-10</sub> (indicated by open squares  $\square$ ) macromediators in bulk at 125°C.



**Figure 5** Normalized gel permeation chromatograms (GPC) of various samples taken during the polymerization of styrene using various poly(lactide) functionalized TEMPO (PLA<sub>T</sub>) mediators in bulk at 130°C using (a) PLA<sub>T</sub>-4, (b) PLA<sub>T</sub>-6, and (c) PLA<sub>T</sub>-10. Molecular characteristics of the PLA<sub>T</sub> mediators are summarized in Table I while molecular weight distribution data of the specific samples presented are summarized in Table III.

lar weight distribution ( $M_w/M_n \sim 1.3$ ), while the distributions corresponding to the higher molecular weight macromediators were somewhat broader with  $M_w/M_n > 1.5$ . The polymerization with the lowest molecular weight macromediator PLA<sub>T</sub>-4 also seemed to have an induction period before the molecular weight started to increase linearly. Such induction times have been observed in TEMPO-mediated polymerizations of styrene<sup>26,33–35</sup> and are attributed to the reduction in nitroxide concentration that occurs when styrene thermally self-initiates. Once sufficient nitroxide is consumed, polymerization effectively commences. With the lower molecular weight PLA<sub>T</sub>-4, its concentration is higher com-

pared to the other macromediators and presumably more TEMPO must be consumed for the styrene polymerization to effectively begin. Future experiments with a wider range of PLA chain lengths attached to TEMPO would confirm the point at which induction periods are significantly reduced.

We repeated the polymerizations using PLA<sub>T</sub>-4 and PLA<sub>T</sub>-10 macromediators and plotted  $M_n$  versus conversion of styrene  $X$  and also  $\ln\left(\frac{1}{1-X}\right)$  versus time  $t$  as shown in Figures 4(a,b). Molecular weight versus conversion was linear over the range of conversions studied for both macromediators and suggests that pseudo-“living” conditions were attained. The apparent induction time observed in the  $M_n$  versus polymerization time plots was less noticeable when plotting  $M_n$  versus styrene conversion and the difference in slopes seems to be proportional to the difference in the target molecular weight of the block copolymer. The plot of  $\ln\left(\frac{1}{1-X}\right)$  versus  $t$  gives the apparent rate constant which is the product of the propagation rate constant  $k_p$  and the concentration of propagating radical species  $[P^*]$ . The plot shown in Figure 4(b) was linear with slopes for both polymerizations nearly the same, thereby indicating that the concentration of propagating radicals was nearly the same for both macromediators.

Gel permeation chromatograms (GPC) of the polymerizations conducted in bulk with the lower target molecular weights (see Fig. 3) are shown in Figure 5 with molecular characteristics summarized in Table III. All three polymerizations show a distinct shift toward higher molecular weight with polymerization time and remained monomodal, despite broadening slightly. At early polymerization times for some of the samples shown in Table III, the copolymer molecular weight was lower compared to the PLA<sub>T</sub> macromediator which may be due to GPC calibration effects. This was confirmed by performing <sup>1</sup>H-NMR on the PLA<sub>T</sub> macromediators which indicated  $M_n$ 's for the PLA<sub>T</sub> macromediators were about 10% lower than that measured by GPC. At longer times, the molecular weight increased and <sup>1</sup>H-NMR confirmed the composition of the block copolymer. Also, the reactions involving the PLA<sub>T</sub>-6 and PLA<sub>T</sub>-10 macromediators commenced almost immediately, whereas the reaction involving the 4 kg/mol macromediator initially went through an induction period lasting about 60 min. A higher target  $M_n$  for the styrene block would likely have decreased the  $M_w/M_n$  by stopping the polymerization earlier and avoiding the termination reactions that inevitably become more prevalent at higher conversions. The polymerizations shown in Figure 4 applied this case and the final  $M_w/M_n$  were slightly narrower compared to the polymerizations shown in Figure 3 with the PLA<sub>T</sub>-4-PS diblock having  $M_w/M_n = 1.44$  and the PLA<sub>T</sub>-10-PS diblock having  $M_w/M_n = 1.41$ . In con-

**TABLE III**  
**Molecular Weight Distribution Data of Poly(styrene)-Poly(lactide) (PS-PLA) Block Copolymers Synthesized by PLA Macromediators at 130°C in Bulk Corresponding to Samples Taken at Various Times Shown in Figure 5**

PS- <i>b</i> -macro-mediator <sup>a</sup>	Chromatogram	Time (min)	$M_n$ (kg/mol) <sup>b</sup>	$M_w$ (kg/mol) <sup>b</sup>	$M_w/M_n$ <sup>b</sup>	$\phi_{PLA}$ <sup>c</sup>
PS-PLA <sub>T</sub> -4 (bulk)	A1	10	4.7	6.6	1.40	0.22
	A2	95	4.7	7.8	1.66	
	A3	193	11.6	14.9	1.28	
PS-PLA <sub>T</sub> -6 (bulk)	B1	10	9.8	16.2	1.65	0.23
	B2	40	11.2	20.2	1.80	
	B3	60	15.4	24.7	1.60	
PS-PLA <sub>T</sub> -10 (bulk)	C1	10	10.5	16.6	1.58	0.26
	C2	45	13.3	21.1	1.59	
	C3	75	16.2	24.6	1.52	

<sup>a</sup> Poly(lactide) functionalized TEMPO mediator (PLA<sub>T</sub>) molecular properties are summarized in Table I.

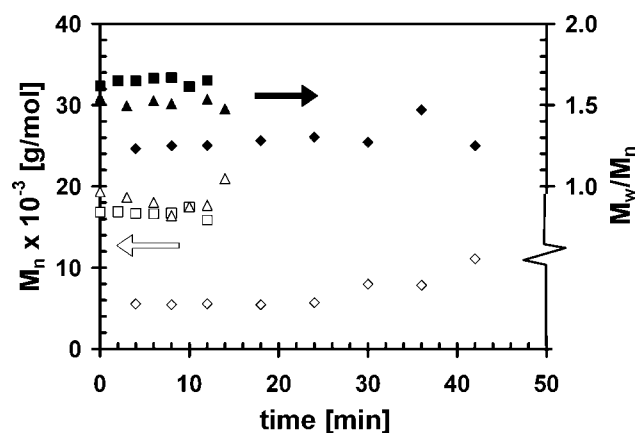
<sup>b</sup> Number average molecular weight  $M_n$ , weight average molecular weight  $M_w$ , and polydispersity index =  $M_w/M_n$  determined using gel permeation chromatography (GPC) relative to poly(styrene) standards in tetrahydrofuran (THF) at 40°C.

<sup>c</sup>  $\phi_{PLA}$  = volume fraction of poly(lactide) (PLA) in the block copolymer as determined by <sup>1</sup>H nuclear magnetic resonance (NMR) in deuterated chloroform (CDCl<sub>3</sub>) and literature data for PS and PLA densities.<sup>30</sup>

trast to polymerizations conducted in bulk, those performed in 50 wt % DMF solution were much slower compared to the bulk polymerization, with very little overall change in the molecular weight of the polymer for the same polymerization times studied for the experiments done in bulk.

#### Polymerization of *tert*-butyl styrene using poly(lactide) functionalized TEMPO (PLA<sub>T</sub>) macromediators

$M_n$  and  $M_w/M_n$  versus time for the polymerization of *t*BuS mediated by the various PLA<sub>T</sub> mediators at 130°C in bulk are shown in Figure 6 while Table IV summarizes the molecular characterization of the PtBuS-PLA diblock copolymers and the PtBuS-PS-



**Figure 6** Number average molecular weight ( $M_n$ ) versus time for the polymerization of *tert*-butyl styrene at 130°C using poly(lactide) functionalized TEMPO macromediators (PLA<sub>T</sub>). (a) PLA<sub>T</sub>-4 in bulk, (b) PLA<sub>T</sub>-6 in 50 wt % dimethylformamide (DMF) solution, and (c) PLA<sub>T</sub>-10 in 50 wt % DMF. Open symbols represent  $M_n$  versus  $t$  data ( $\diamond$  = PLA<sub>T</sub>-4,  $\blacksquare$  = PLA<sub>T</sub>-6,  $\triangle$  = PLA<sub>T</sub>-10) and filled symbols represent polydispersity index ( $M_w/M_n$ ) versus time data.

PLA triblocks derived from them. Similar to the polymerization of styrene using the same macromediators, the *t*BuS bulk polymerizations rapidly became viscous and samples taken at the designated initial time of polymerization were already higher in molecular weight than those for the identical styrene polymerizations with the same mediators. For example, using the 4 kg/mol macromediator, the polymerization time to achieve nearly the identical block copolymer molecular weight was about four times less with *tert*-butyl styrene compared to styrene. The effect of *para*-substituents on styrenic monomers has been studied for conventional radical polymerization<sup>36,37</sup> and atom transfer radical polymerization (ATRP)<sup>38</sup> using the Hammett relationship<sup>39</sup> which suggests the propagation rate constant increases as the electron withdrawing group becomes stronger in the *para*-position. Based on the Hammett principle, *tert*-butyl styrene is electron-donating and should have a lower propagation rate constant compared to styrene although there is some debate over the applicability of the Hammett relationship to controlled free radical polymerization.<sup>38</sup> For *para*-substituted styrenes using Ziegler-Natta catalysts, reactivity of *tert*-butyl styrene was enhanced compared to styrene.<sup>40</sup> The experiments of Catala and coworkers did not indicate a significant difference in the apparent rate constant for the polymerization of *tert*-butyl styrene<sup>41</sup> and styrene<sup>42</sup> using a hindered di-*tert*-butyl nitroxide mediator. We are currently attempting to confirm the difference in apparent reactivity between styrene and *tert*-butyl styrene using similar nitroxide mediated polymerizations without the complicating factor of the various PLA macromediators. The molecular weight distributions were however quite similar to those obtained from the polymerization of styrene. The narrowest distribution for the PtBuS-PLA diblock was obtained using the 4 kg/mol macrome-



**TABLE IV**  
**Molecular Characteristics of Poly(*tert*-butyl styrene)-Poly(lactide) (PtBuS-PLA) Block Copolymers Mediated by Poly(lactide) Functionalized TEMPO Macro-mediators in Bulk at 130°C**

Precursor diblock/triblock copolymer	Macromediator <sup>a</sup>	$t_{\text{polym.}}$ (min)	$M_n$ (kg/mol) <sup>b</sup>	$M_w$ (kg/mol) <sup>b</sup>	$M_w/M_n$ <sup>b</sup>	$\phi_{\text{PLA}}$ <sup>c</sup>
PtBuS-PLA <sub>T</sub> -4/ PtBuS-PS-PLA <sub>T</sub> -4 (bulk)	PLA <sub>T</sub> -4	42	11.1	13.9	1.25	0.33
PtBuS-PLA <sub>T</sub> -6/ PtBuS-PS-PLA <sub>T</sub> -6 (DMF)	PLA <sub>T</sub> -6	12	15.8	26.2	1.65	0.17
PtBuS-PLA <sub>T</sub> -10/ PtBuS-PS-PLA <sub>T</sub> -10 (DMF)	PLA <sub>T</sub> -10	3	28.5	48.1	1.69	0.10
		14	21.0	30.9	1.47	0.19
		5	28.1	43.2	1.54	0.17

<sup>a</sup> Molecular characteristics of poly(lactide) functionalized TEMPO macromediators (PLA<sub>T</sub>) summarized in Table I.

<sup>b</sup> Number average molecular weight ( $M_n$ ), weight average molecular weight ( $M_w$ ), and polydispersity index ( $M_w/M_n$ ) measured using gel permeation chromatography (GPC) relative to poly(styrene) standards in tetrahydrofuran (THF) at 40°C.

<sup>c</sup>  $\phi_{\text{PLA}}$  = volume fraction of poly(lactide) (PLA) in the block copolymer as determined by <sup>1</sup>H nuclear magnetic resonance (NMR) in deuterated chloroform (CDCl<sub>3</sub>).

diator ( $M_w/M_n \sim 1.3$ ), while the distributions corresponding to the higher molecular weight macromediators were slightly broader ( $M_w/M_n \sim 1.5$ ) as was the case for the PS-PLA blocks. For the *tert*-BuS polymerizations with the higher molecular macromediators, bulk polymerizations were much faster and were more readily conducted in DMF solution.

#### Chain extension of poly(*tert*-butylstyrene)-poly(lactide) (PtBuS-PLA) Diblocks with styrene

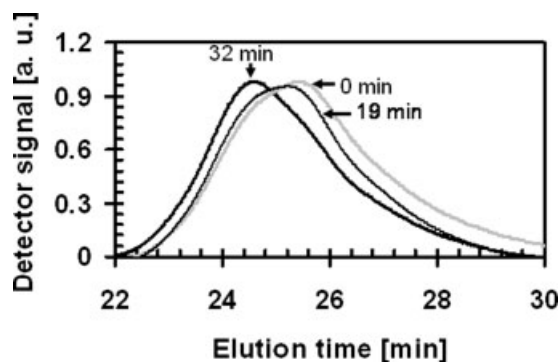
Once the PtBuS-PLA<sub>T</sub> diblock copolymers were synthesized, the addition of a PS block was pursued to check the "livingness" of the chains and to produce the desired ABC precursor triblock copolymer. The diblock copolymers were reinitiated with BPO and sufficient styrene so that the molecular weight of the PS block would be relatively short with  $M_n \sim 5$  kg/mol (corresponding to 50 mol % of the styrene added). Very little PS was required since we desired to produce a relatively short segment. As mentioned previously, the polymerization with *t*BuS was rapid, even when diluted in DMF solvent at a temperature of 120°C. In all cases, the molecular weight distribution broadened with  $M_w/M_n > 1.5$  for all the macromediators used as shown in Table IV but remained relatively monomodal. After the styrene was added, polymerizations were rapid with more than sufficient styrene being incorporated as indicated by <sup>1</sup>H-NMR. Using PLA<sub>T</sub>-6 macromediator, 39 mol % styrene was incorporated into the styrenic matrix block while when using PLA<sub>T</sub>-4 ( $M_n \sim 6$  kg/mol), 65 mol % styrene was incorporated into the styrenic matrix block. Thus, the polymerization was rapid when adding the styrene to the PtBuS-PLA<sub>T</sub> with a higher incorporation of styrene than desired. The polymerization rate could

have been adjusted by lowering the temperature or making the solution more dilute. However, the intermediate step of recovering the PtBuS-PLA<sub>T</sub> macroinitiator to start the polymerization of the PS block was deemed to be cumbersome for potential scale-up and we then tested the applicability of tapering a PS block after polymerization of a pure PtBuS was initiated with the appropriate PLA<sub>T</sub> mediator.

#### Addition of poly(styrene) to poly(*tert*-butylstyrene)-poly(lactide) diblocks by tapering

The alternative strategy to synthesize the triblock copolymer sequentially was to implement a tapering of the PS block by first polymerizing *t*BuS using the PLA<sub>T</sub> macromediator and then injecting styrene to produce the P(*t*BuS)-P(*t*BuS-*ran*-S)-PLA tapered triblock copolymer. The amount of styrene incorporated was estimated from the reactivity ratios for the conventional random free radical copolymerization of *tert*-butylstyrene with styrene which are  $r_{\text{tBuS}} = 1.581$  and  $r_S = 0.774$ , respectively.<sup>43</sup> The higher reactivity ratio for *t*BuS indicates that the random block will incorporate a slightly larger amount of *t*BuS than S for a given feed concentration.

The tapering method was used only with the higher molecular weight PLA-functionalized TEMPO macromediators (PLA<sub>T</sub>-6 and PLA<sub>T</sub>-10). The same formulations for synthesizing the PtBuS-PLA<sub>T</sub> diblocks were used and the reaction temperature was lowered to 120°C using 50 wt % DMF as the solvent. GPC chromatograms of samples taken during the polymerization before styrene injection and at the conclusion of the polymerization are shown in Figure 7 when using the PLA<sub>T</sub>-6 macromediator while the molecular characteristics of the experi-



**Figure 7** Gel permeation chromatograms (GPC) taken of tapered poly(*tert*-butyl styrene)-poly(*tert*-butyl styrene-*r*-styrene)-poly(lactide) (PtBuS-P(*t*BuS-*r*-S)-PLA) block copolymers at 0 min polymerization (taken as when the temperature reached 120°C) and 32 min polymerization at 120°C in 50 wt % dimethylformamide (DMF) solution. The poly(lactide) functionalized TEMPO macromediator PLA<sub>T</sub>-6 was used which had a number average molecular weight  $M_n = 7.4$  kg/mol, weight average molecular weight  $M_w = 9.2$  kg/mol, and polydispersity index  $M_w/M_n = 1.24$ . Before styrene injection at  $t = 19$  min,  $M_n = 11.8$  kg/mol,  $M_w = 17.2$  kg/mol, and  $M_w/M_n = 1.58$ . After injection of styrene at  $t = 19$  min, the chromatogram shifted to higher molecular weights while still retaining a monomodal molecular weight distribution. After 32 min, the sample had  $M_n = 13.7$  kg/mol,  $M_w = 21.1$  kg/mol, and  $M_w/M_n = 1.58$ .

ments using both macromediators are summarized in Table V. The molecular weight distribution did not change significantly after the styrene injection with only a short random block of *t*BuS/S being incorporated  $\sim 2$  kg/mol. <sup>1</sup>H-NMR from the final samples indicated that very little styrene was incorporated as expected (<10%). Estimation of the incorporation of styrenic units was also done given the monomer loadings, molecular weight data from GPC, and the literature reactivity ratios for the *t*BuS/S random free radical copolymerization. For example, when using PLA<sub>T</sub>-6 and knowing the degree of polymerization of *t*BuS incorporated from <sup>1</sup>H-NMR and GPC data before styrene injection, the

molar monomer feed fraction of *t*BuS when the styrene was added was  $f_{tBuS,0} = 38$  mol %. Similarly for the polymerization using PLA<sub>T</sub>-10,  $f_{tBuS,0} = 45$  mol %. Assuming that compositional drift after styrene injection could be ignored since the conversion was kept relatively low, the Mayo-Lewis relationship given by eq. (1)<sup>44</sup> could be used to determine the copolymer composition with respect to *t*BuS,  $F_{tBuS}$ , given the reactivity ratios  $r_{tBuS} = 1.581$  and  $r_S = 0.774$  for *t*BuS and styrene,<sup>43</sup> respectively, and assuming a terminal reactivity model holds.

$$F_{tBuS} = \frac{r_{tBuS}f_{tBuS}^2 + f_{tBuS}(1 - f_{tBuS})}{r_{tBuS}f_{tBuS}^2 + 2f_{tBuS}(1 - f_{tBuS}) + r_S(1 - f_{tBuS})^2} \quad (1)$$

Note that  $f_{tBuS} \approx f_{tBuS,0}$  in eq. (1). Consequently, the copolymer compositions in the short, random *t*BuS/S segment determined using eq. (1) gave  $F_{tBuS} = 46$  mol % for the system using PLA<sub>T</sub>-6 and  $F_{tBuS} = 54$  mol % for the system using PLA<sub>T</sub>-10. Overall, the total incorporation of styrene calculated was thus 17–18 mol % in both cases, in generally good agreement with <sup>1</sup>H-NMR data of the final copolymers. Thus, tapering of the second PS segment into the PtBuS segment is possible and we are now examining in more detail how to incorporate PtBuS/PS segments of varying composition into such blocks and then selectively converting the PS segments to segments with desired functional groups.

## CONCLUSIONS

The polymerization of styrene and *tert*-butyl styrene was examined by nitroxide-mediated polymerization using poly(lactide) functionalized TEMPO macromediators (PLA<sub>T</sub>) synthesized by ring-opening polymerization. All PLA<sub>T</sub> macromediators were characterized by relatively narrow molecular weight distributions (polydispersities varying from 1.19 to 1.26) and number average molecular weights  $M_n$  from 6.1 to 11.3 kg/mol according to GPC with PS standards or 5.4 to 10.5 kg/mol according to <sup>1</sup>H-NMR. For

**TABLE V**  
Characteristics of Poly(*tert*-butyl styrene)-tapered-Poly(styrene)-Poly(lactide) Block Copolymers (PtBuS-P(*t*BuS-*r*-S)-PLA) Synthesized at 120°C in 50 wt % Dimethylformamide (DMF) Solution

Experiment	$t_{\text{polym}}$ (min)	$M_n^a$ (kg/mol)	$M_w^a$ (kg/mol)	$M_w/M_n^a$
PtBuS-PLA <sub>T</sub> -6 (before styrene injection)	12	11.9	18.9	1.59
PtBuS-P( <i>t</i> BuS- <i>r</i> -S)-PLA <sub>T</sub> -6 (completion)	32	13.7	21.1	1.54
PtBuS-P( <i>t</i> BuS- <i>r</i> -S)-PLA <sub>T</sub> -10 (before styrene injection)	12	14.7	22.4	1.52
PtBuS-P( <i>t</i> BuS- <i>r</i> -S)-PLA <sub>T</sub> -10 (completion)	38	16.8	25.5	1.52

<sup>a</sup> Number average molecular weight  $M_n$ , weight average molecular weight  $M_w$ , and polydispersity index =  $M_w/M_n$  determined using gel permeation chromatography (GPC) relative to poly(styrene) standards in tetrahydrofuran (THF) at 40°C.

both styrene and *tert*-butyl styrene, polymerizations using the lowest molecular weight PLA<sub>T</sub> mediator (PLA<sub>T</sub>-4) in bulk at 130°C resulted in narrow molecular weight distributions (polydispersities = 1.25–1.29) while polymerizations mediated with the higher molecular weight mediators (PLA<sub>T</sub>-6 and PLA<sub>T</sub>-10) resulted in block copolymers with broader molecular weight distributions (polydispersities = 1.47–1.65).  $M_n$  of the block copolymer increased with time in a linear fashion within the time scales studied, indicating pseudo-“living” conditions were achieved. Polymerizations became rapidly viscous with the higher molecular weight mediators and were about three times faster using *tert*-butyl styrene compared to styrene. Chain extension of poly(*tert*-butyl styrene)-poly(lactide) (PtBuS-PLA) diblocks with styrene (S) to produce PtBuS-PS-PLA triblocks indicated the PtBuS-PLA was effective in reinitiating the polymerization with a monomodal product with relatively broad molecular weight distributions and a very rapid rate of styrene incorporation, typically taking only a few minutes at 130°C to add a PS segment ~10 kg/mol. A tapering strategy of injecting styrene to a solution containing growing chains of P(*t*BuS)-PLA was also tested using the two higher molecular weight PLA<sub>T</sub> mediators at a lower temperature of 120°C and 50 wt % dimethylformamide (DMF) solvent. Incorporation of short random *t*BuS/S blocks was achieved with styrene incorporation ~17–18 mol % styrene relative to *tert*-butyl styrene and relatively narrow molecular weight distributions (polydispersities ~1.5). These results allow the development of ABC PtBuS-PS-PLA triblock copolymer precursors for introduction of functional groups selectively onto the PS segments after suitable conversion.

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