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Synthesis and characterization of A–B–A triblock copolymers derived from chloro-telechelic poly(L-lactide): combining ring-opening polymerization (ROP) and atom transfer radical polymerization (ATRP)

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Abstract

Ring-opening polymerization (ROP) of L-lactide was combined with atom transfer radical polymerization (ATRP) to produce well-defined linear block copolymers. Poly(L-lactide) (PLLA) was synthesized via ROP using ethylene glycol as an initiator and stannous octoate as a catalyst. The isolated hydroxy-telechelic PLLA was reacted with thionyl chloride and pyridine in toluene to afford chloro-telechelic PLLA (Cl-PLLA-Cl). The latter was employed as a macroinitiator in the synthesis of A–B–A triblock copolymers having either *tert*-butyl acrylate or benzyl acrylate outer blocks. Outer-block molecular weight was targeted by the mole ratio of monomer (acrylate) to the PLLA chloride initiating sites. The actual incorporation of acrylate into the triblock copolymer was lower than the molar feed ratio as the copolymer became increasingly less soluble upon conversion of acrylate in all cases.

Keywords: Ring-opening polymerization; Atom transfer radical polymerization; Llactide

1. Introduction

Efforts to design polymer materials with new properties are directly associated with the precise control of polymer architecture. Recent advances in graft and block copolymer synthesis have generated a significant interest in combining polymerization techniques such as ring-opening (ROP) and atom transfer radical polymerization (ATRP) [1–5]. For example, Liu and Baker were the first authors to utilize ROP and ATRP in a manner to produce linear block copolymers consisting of L-lactide and methoxy-capped oligo(ethylene oxide) methacrylate (OEGMA) blocks. The authors used the heterofunctional initiator, 3-hydroxy-2,2-dimethylpropyl 2-bromo-2-methylpropionate, to first initiate L-lactide from the hydroxy end followed by OEGMA from the bromo terminus [2]. Lee and co-workers were the first to report the synthesis and degradation analysis of chloride-terminated PLLA using thionyl chloride and pyridine [6]. The authors fashioned mono-, tri-, and tetra-chloro PLLAs derived from dodecanol-, glycerol-, and pentaerythritol-initiated PLLAs, respectively. Although this was the first report of chloride end-functionalized PLLA, the authors did not utilize the end-functionalized polymers in any post-polymerization modification. The end groups of chloride-terminated PLLA bear a secondary halide that is beta to a carbonyl group. Such structures are known to be efficient initiators for ATRP of acrylates. Thus chloro-telechelic PLLA was used as a macroinitiator for ATRP of *tert*-butyl acrylate and benzyl acrylate, to create novel block copolymers. In this communication, we report the synthesis of poly(L-lactide)-polyacrylate block copolymers in which the polylactide is directly attached to the acrylate block without the use of a linking molecule.

2. Experimental section

2.1. Materials

L-lactide, a gift from Ortec, Inc., ethylene glycol (99.8% anhydrous, Aldrich), tin (II) ethylhexanoate (95%, Aldrich), copper (I) chloride (99%, Aldrich) and pyridine (99.8%

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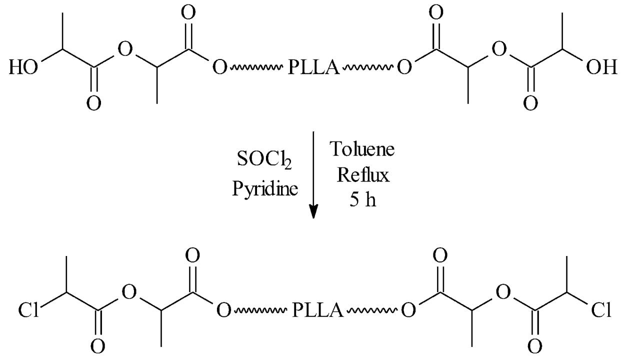


Scheme 1. Synthesis of chloro-telechelic PLLA from hydroxy-telechelic PLLA using thionyl chloride in the presence of pyridine.

anhydrous, Aldrich) were transported into a VAC glove box, stored in a dry nitrogen environment, and used as received. Toluene (Aldrich) was refluxed with sodium for 24 h and distilled under dry nitrogen prior to use. Thionyl chloride was distilled from 10% (w/w) triphenyl phosphite and stored under dry nitrogen prior to use. Chlorotrimethylsilane (99 + %, redistilled, Aldrich) was used to silanize all glassware prior to use. *tert*-Butyl acrylate (98%, Aldrich) and benzyl acrylate (98%, Aldrich) were degassed via three consecutive freeze-pump-thaw cycles prior to use. *N*,*N*,*N*′,*N*″,*N*″-Pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich) was degassed by sparing with dry nitrogen for ca. 10 min prior to use.

2.2. Instrumentation

Molecular weights and molecular weight distributions

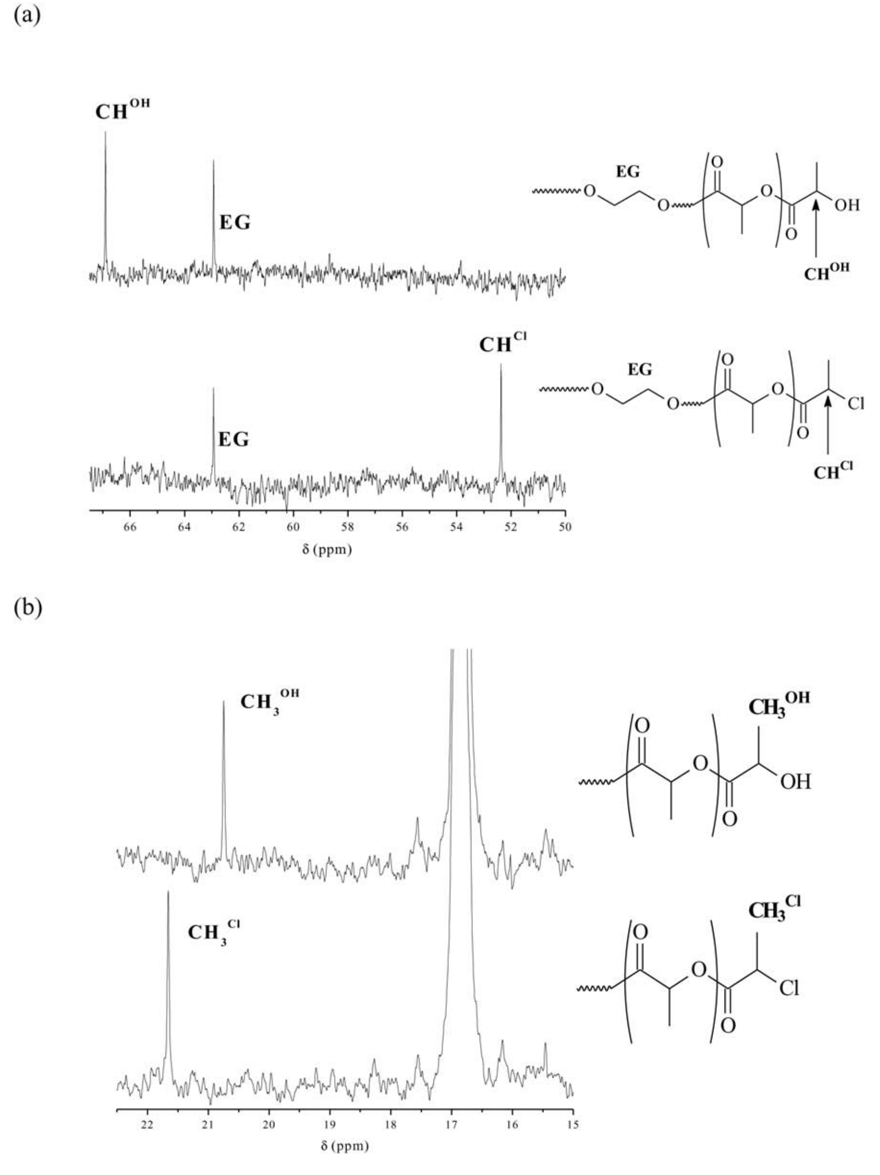
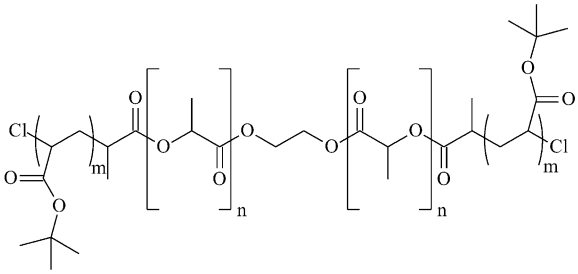
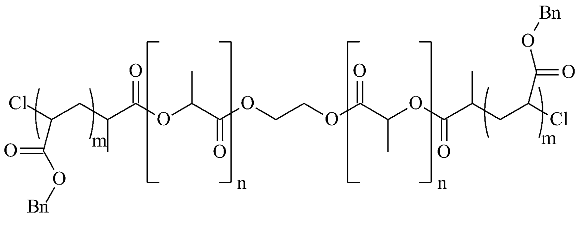


Fig. 1. ^{13}C NMR comparisons of hydroxy-terminated PLLA and chloride-terminated PLLA with respect to the methine (a) and methyl (b) regions.



Poly(benzyl acrylate-*b*-L-lactide-*b*-benzyl acrylate)



Bn = CH_2Ph

Fig. 2. Poly(*tert*-butyl acrylate-*b*-LLA-*b*-*tert*-butyl acrylate) and poly (benzyl acrylate-*b*-LLA-*b*-benzyl acrylate) structures produced via ATRP of *tert*-butyl acrylate and benzyl acrylate, respectively, using a chloro-telechlelic PLLA macroinitiator.

were determined using a gel permeation chromatography (GPC) system equipped with a Wyatt Technology mini-DAWN on-line MALLS detector as described previously [7]. Solution ^{1}H and ^{13}C NMR were obtained on a Varian Mercury-300 or a Varian Mercury-500 spectrometer using 5 mm o.d. tubes with sample concentrations of 5 and 10% (w/v), respectively, using chloroform-*d* ($CDCl_3$) as solvent with internal standard tetramethylsilane (TMS). A Bruker Equinox™ 55 FTIR spectrometer equipped with an Axiom Analytical Diamond ATR Probe (DMD-270) and an external MCT mid band detector was used to monitor conversion of L-lactide monomer by following the disappearance of the peaks at 1240 and 933 cm^{-1} [8]. Thermal analysis was performed using a TA Instruments DSC Q1000 under a nitrogen atmosphere. Samples (~7 mg) were initially cooled to −50 °C, then heated from −50 to 180 °C at 10 °C/min, quenched to −50 °C, and finally reheated to 180 °C (10 °C/min). The glass transition temperatures were reported as the midpoint of the endotherm from the second heating in the DSC experiments.

2.3. Procedures

2.3.1. Synthesis of hydroxy-terminated PLLA

A silanized 500 mL 4-neck round-bottom flask was charged with 0.775 g (0.0125 mol) ethylene glycol, 206.467 g (1.4324 mol) L-lactide, and 192 mL of toluene. Each joint was capped with a rubber septum, and the reaction vessel was removed from the glove box and placed into a fume hood. After the acquisition of a toluene background (average of 64 scans), the reaction vessel was carefully connected to the ATR probe using a dry nitrogen purge to avoid contact with the atmosphere. Furthermore, a condenser was fitted to the reaction vessel under a constant dry nitrogen purge was established and a thermocouple was inserted into the reaction vessel through a rubber septum to record the temperature of the polymerizing medium. An oil bath set to 95 °C was raised to entirely submerge the contents of the flask. Upon dissolution of monomer, data collection commenced, and spectra were recorded every 5 min as the average of 16 scans. During this equilibration time, a syringe was filled with stannous octoate within the dry box and placed into a dessicator. The dessicator was subsequently removed from the dry box and immediately weighed. Once the system was stable as determined by the constant IR spectrum and constant temperature, 1.236 g (3.051×10^{-3} mol) of stannous octoate, measured by difference, was injected into the reaction vessel to commence polymerization. Monomer conversion was monitored by the disappearance of the 1240 and 933 cm^{-1} peaks associated with the C–O–C stretch and ring-breathing mode of the cyclic monomer, respectively. Once the 933 cm^{-1} peak flattened into the baseline, the polymerization was terminated by lowering the oil bath, removing the reaction vessel from the probe, and subsequently immersing the flask into liquid nitrogen. The polymer solution was allowed to equilibrate to room temperature and then concentrated under reduced pressure. The concentrated polymer was dissolved in methylene chloride and precipitated into a 4-fold excess of methanol. The isolated

Table 1
Reaction conditions for triblock copolymer syntheses using chloro-telechelic PLLA as a macroinitiator

Experiment	[Initiator][a] $\times10^2$ (mol/L)	Monomer	[Monomer] (mol/L)	[CuCl]$\times10^4$ (mol/L)	[CuCl]:[PMDETA]	Time (h)
1	2.05	*t*-BA	1.85	1.82	[1:1]	10
2	1.96	*t*-BA	2.94	3.33	[1:1]	15
3	3.27	BnA	3.37	3.33	[1:1]	24
4	2.19	BnA	4.49	2.53	[1:1]	48

All polymerizations were performed in ~10 mL of toluene and concentrations are reported in molarity. *t*-BA = *tert*-butyl acrylate; BnA = benzyl acrylate; CuCl = cuprous chloride; PMDETA = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine

[a] Chloro-telechelic PLLA with $M_n = 14{,}400$ g/mol and PDI = 1.08 was employed as the macroinitiator in all formulations.

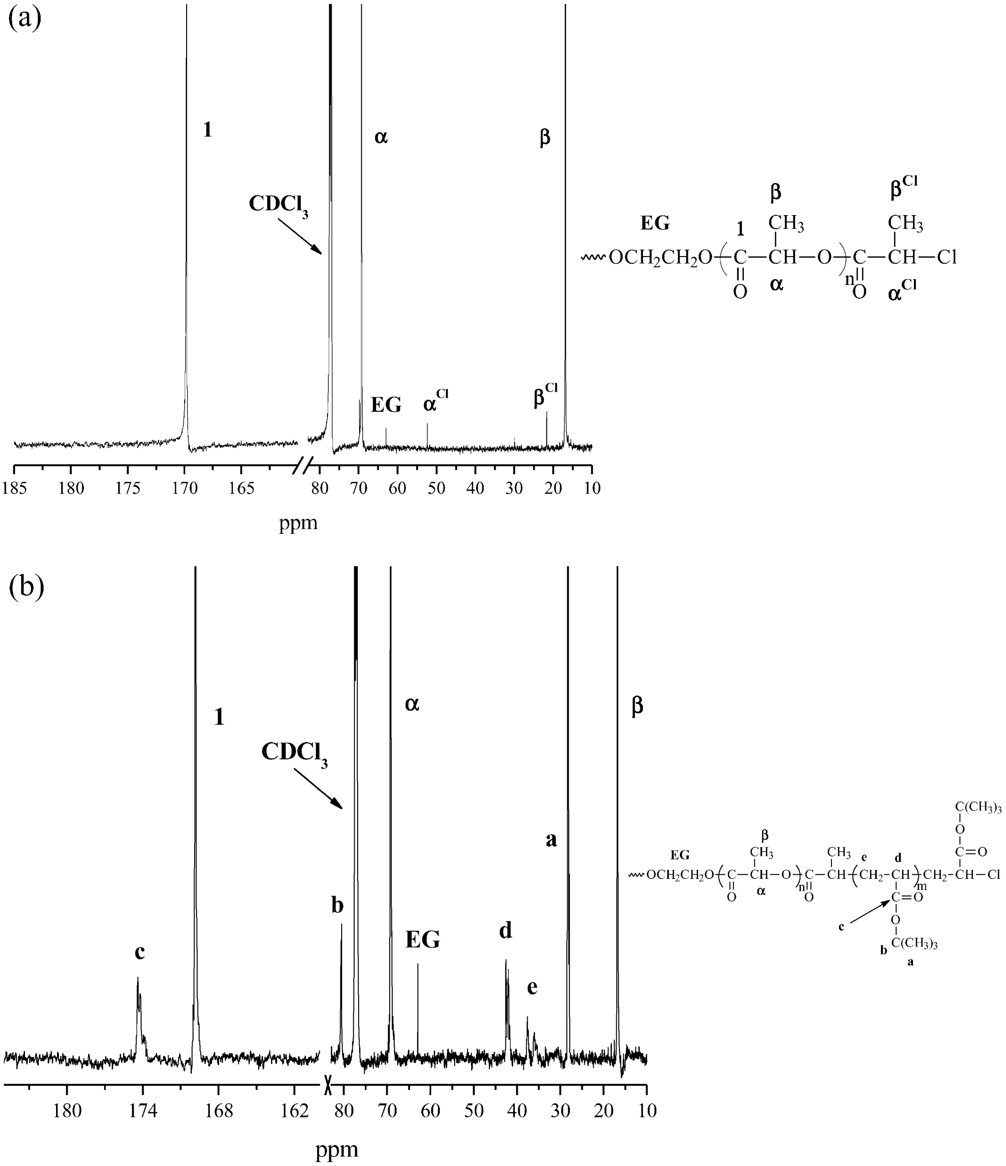


Fig. 3. ^{13}C NMR spectra of chloro-telechelic PLLA (a) and poly(*tert*-butyl acrylate-*b*-LLA-*b*-*tert*-butyl acrylate) (b) (Experiment 1, Table 2).

polymer was filtered and dried overnight in a vac oven at 60 °C prior to analysis.

2.3.2. Synthesis of chloride-terminated PLLA

A silanized 250 mL 2-neck round-bottom flask was charged with a magnetic stirrer, 27.0 g (1.88 mmol) hydroxyl-terminated PLLA, and 150 mL toluene. The reaction flask was immersed in a 100 °C oil bath to dissolve the polymer. After dissolution of the PLLA, 0.455 g (5.75×10^{-3} mol) of pyridine was added and the system was allowed to equilibrate for ~3 min. In the meantime, 0.407 g (3.45×10^{-3} mol) thionyl chloride was combined with 10 mL of toluene in a pressure-equalizing addition funnel within the dry box. The thionyl chloride solution was removed from the dry box, connected to the reaction vessel, and purged with nitrogen. Next, the thionyl chloride solution was added dropwise to the PLLA solution over ~15 min. After addition of the thionyl chloride, the contents of the flask were allowed to react for 4.5 h at ~95 °C. The polymer solution was allowed to cool to room temperature, filtered to remove pyridinium hydrochloride, and subsequently evaporated under vacuum to remove toluene. The concentrated polymer was dissolved in chloroform and washed 3x with distilled water. The organic layer was then dried overnight using $Mg(SO_4)$ and later filtered. Finally, the polymer solution was precipitated into a 4-fold excess of methanol, filtered, and dried in a vacuum oven at 60 °C prior to analysis.

2.3.3. Block copolymer synthesis via ATRP

Chloro-telechelic PLLA (2.955 g, 2.052×10^{-4} mol), cuprous chloride (0.018 g, 1.8×10^{-4} mol), toluene

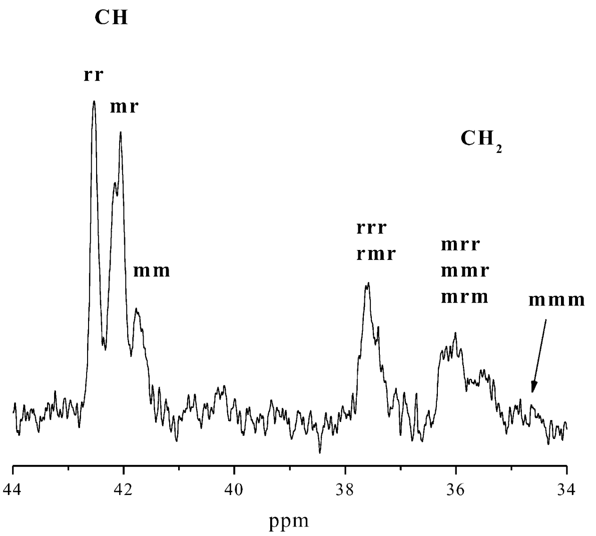


Fig. 4. ^{13}C NMR spectrum of the methine and methylene carbon region with respect to the *tert*-butyl acrylate block of poly(*t*BA-*b*-LLA-*b*-*t*BA) (Experiment 1, Table 1). The spectrum demonstrates a syndiotactic-rich *tert*-butyl acrylate block.

(10 mL), and *tert*-butyl acrylate (2.7 mL, 1.9×10^{-2} mol) were combined in a 50 mL one-neck round-bottom flask within a drybox. The flask was capped with a rubber septum, transported to a fume hood, and subsequently submerged in a constant-temperature oil bath at 95 °C to dissolve the Cl-PLLA-Cl. The flask was then transferred to a dry ice/acetone bath to freeze the contents, whereupon vacuum was applied for ca. 10 min. Vacuum was subsequently removed, and the flask was again submerged in a constant temperature oil bath at 95 °C. This freeze-pump-thaw process was repeated for a total of three cycles at which point PMDETA (0.038 mL, 1.8×10^{-4} mol) was injected through the rubber septum, to initiate polymerization of *tert*-butyl acrylate. The reaction contents were allowed to react at 90 °C for at least 10 h. The copolymers became increasingly less soluble and eventually solidified at the bottom of the flask. The reaction vessel was then removed from the oil bath and dissolved in ca. 60 mL methylene chloride. The dark green solution was then passed through a 30 cm column packed with basic alumina to remove residual copper catalyst, rendering the solution colorless. The colorless solution was then precipitated into a 4-fold excess of hexanes, filtered, and dried overnight in vacuo.

Table 2
Molecular weight characteristics and molar incorporation of acrylates into acrylate-*b*-lactide-*b*-acrylate triblock copolymers

Experiment	$M_{n,\text{SEC-MALLS}}$	PDI	% Acrylate$_{\text{Theo}}$[a]	% Acrylate$_{\text{Expt}}$[b]
A	14,400	1.08	0	0
1	19,100	1.48	47.4	15.9
2	24,200	1.38	60.1	19.3
3	18,900	1.35	67.2	10.2
4	23,300	1.11	50.8	12.6

Experiment A refers to the chloride-telechelic PLLA macroinitiator. PDI, polydispersity index

[a] Theoretical percent acrylate determined using the following equation:

$$\%\ \text{Acrylate}_{\text{theo}} = \frac{\text{mol Acrylate}}{\text{mol Acrylate} + \text{mol LLA}},$$

where mol Acrylate = mass acrylate/molar mass acrylate and mol LLA = mass PLLA/144.14 g/mol.

[a] Experimental percent acrylate incorporated into the triblock copolymer was determined using ^{1}H NMR spectroscopy.

3. Results and discussion

To facilitate the synthesis of a block copolymer consisting of a PLLA innerblock and either a *tert*-butyl acrylate or a benzyl acrylate outerblock, hydroxy-telechelic PLLA was first transformed to chloro-telechelic PLLA. Following the procedure described by Lee et al. [6], hydroxy-telechelic PLLA was reacted with thionyl chloride and pyridine in toluene as shown in Scheme 1. The chloride-terminated PLLA was characterized using ^{1}H and ^{13}C NMR spectroscopy. Fig. 1 shows the ^{13}C NMR spectra of the hydroxy- and chloro-telechelic PLLA. The conversion of the hydroxyl groups to the chloride terminal moieties was characterized by two significant chemical shifts. The terminal methine (*C*H–OH) in the hydroxy-terminated PLLA shifted from 66.9 to 52.4 ppm when converted to the chloride-terminated species (*C*H–Cl) (Fig. 1(a)). In addition, the terminal methyl group shifted from 20.7 ppm in the hydroxy-terminated PLLA (CH$_3$–OH) to 21.7 ppm in the chloride terminated PLLA (CH$_3$–Cl) (Fig. 1(b)). Furthermore, the main chain PLLA peaks and the ethylene glycol initiator peak (labeled EG in Fig. 1(a)) remained unchanged between the spectra.

3.1. Chloro-telechelic PLLA as a macroinitiator in ATRP synthesis tert-butyl acrylate and benzyl acrylate

Matyjaszewski and Xia demonstrated the use of *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) as an efficient ligand for the polymerization of styrene, methyl methacrylate, and methyl acrylate in an earlier report [9]. Due to their success, PMDETA was used as the ligand in this study in the presence of cuprous chloride to synthesize triblock copolymers consisting of a PLLA inner block and *tert*-butyl acrylate or benzyl acrylate outer blocks. The structures of the resulting copolymers are shown in Fig. 2. Table 1 lists the reaction conditions used in the triblock syntheses. Polymerization was conducted under a blanket of nitrogen at 90 °C for at least 10 h. The triblock copolymers were isolated and characterized using ^{1}H and ^{13}C NMR spectroscopy, and SEC-MALLS.

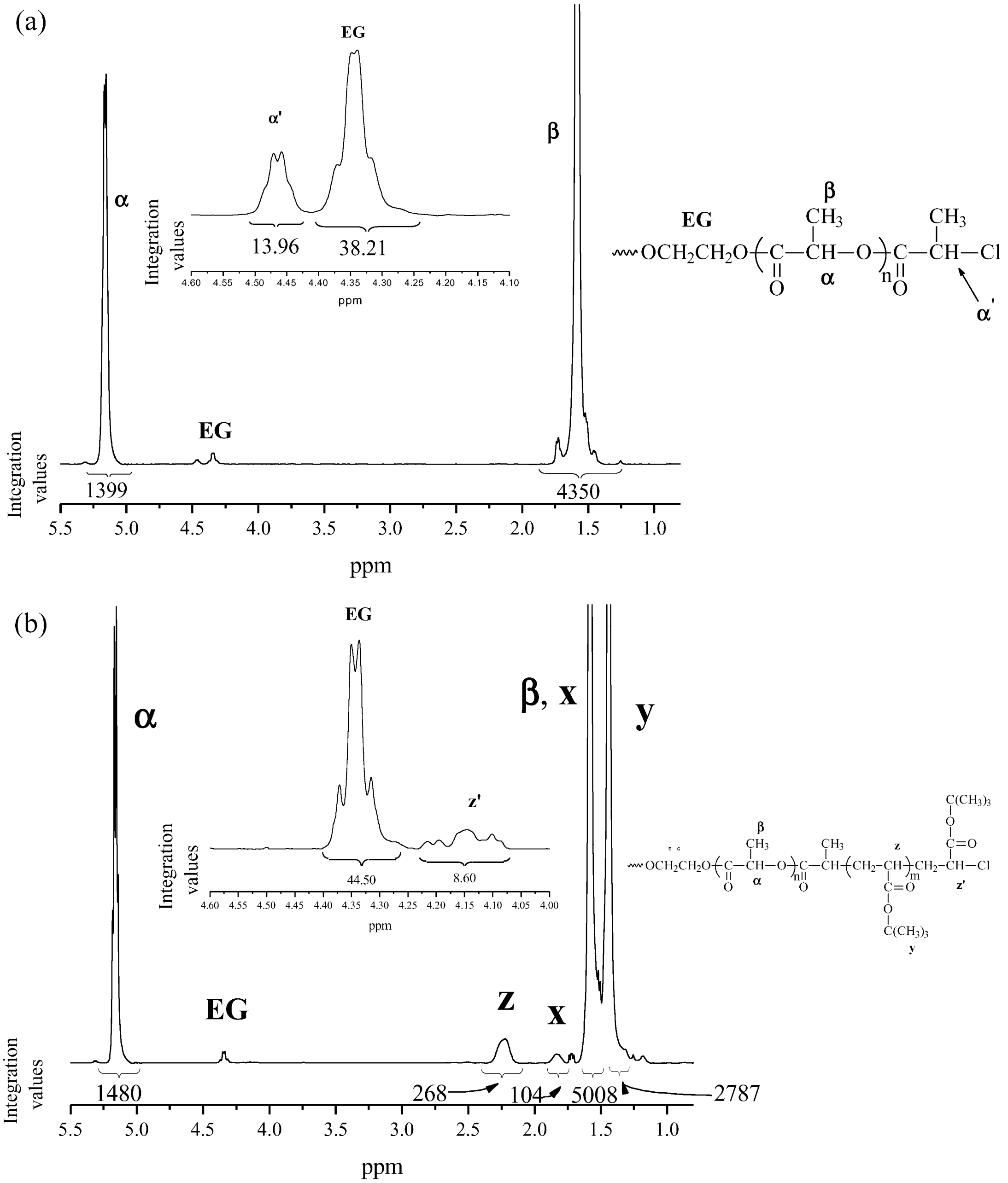


Fig. 5. ^{1}H NMR spectra of chloro-telechelic PLLA (a) and poly(*tert*-butyl acrylate-*b*-LLA-*b*-*tert*-butyl acrylate) (b) (Experiment 1, Table 2).

3.2. Poly(tert-butyl acrylate-b-L-lactide-b-tert-butyl acrylate) synthesis and characterization

Fig. 3 displays an overlay of carbon NMR spectra showing the incorporation of poly(*t*-butyl acrylate) onto the chloride chain end of the PLLA. Examination of the spectra shows the disappearance of the terminal methyl carbon (21.7 ppm, β^{Cl}) and the terminal methine carbon (52.4 ppm, α^{Cl}) from the chloro-telechelic PLLA (Fig. 3(a)) upon polymerization of *tert*-butyl acrylate (Fig. 3(b)); the absence of these peaks indicates quantitative initiation by the chloride chain end within the limits of detection of the ^{13}C NMR spectrometer (Varian Mercury 500). Furthermore, the spectra demonstrate retention of main chain PLLA carbon resonances at 16.8 ppm (methyl, β), 69.1 ppm (methine, α), and 169.6 ppm (carbonyl, 1), and the appearance of peaks at 28.3, 80.5 and 174.4 ppm, which were attributed to the main chain methyl (a), pendent quaternary (b), and carbonyl (c) carbon resonances of the *tert*-butyl acrylate block, respectively. The peak at 62.9 ppm, which was attributed to the original ethylene glycol initiator fragment, is evident in both spectra. Also, the broad peaks at 35.2–36.4 and 41.8–42.4 ppm were attributed to the main chain methylene (e) and methine (d)

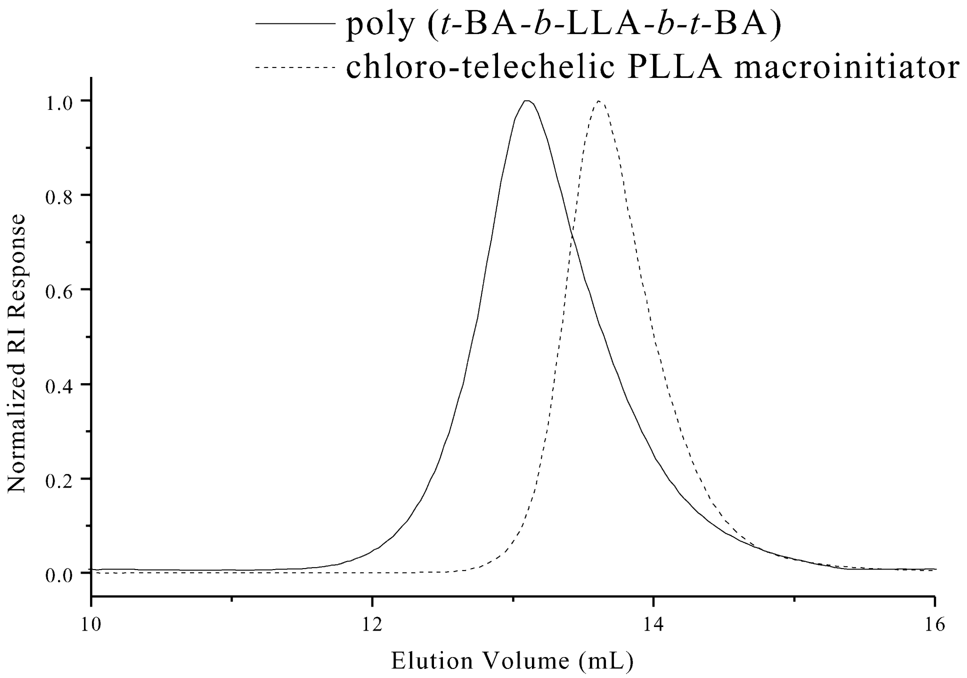


Fig. 6. SEC-MALLS chromatograms for chloro-telechelic PLLA ($M_n = 14{,}400$ g/mol, PDI = 1.08) (Experiment A, Table 2) and poly(*tert*-butyl acrylate-*b*-LLA-*b*-*tert*-butyl acrylate) ($M_n = 19{,}100$ g/mol, PDI = 1.48) (Experiment 1, Table 2).

carbon resonances of the *tert*-butyl acrylate block, respectively. Broadening of these signals was attributed to tacticity resulting from the bulky, pendent *tert*-butyl groups [10,11]. The methine (41–44 ppm) and methylene (34–38 ppm) carbon regions of the *tert*-butyl acrylate block (Experiment 1, Table 1) shown in Fig. 4 shows that the *tert*-butyl acrylate block is syndiotactic-rich based on assignments made by Liu et al. [10]. The relative intensities of the *rr* and *mr* triads of the methine carbon and the *rrr* and *rmr* tetrads, respectively, indicate that *tert*-butyl acrylate adds to a growing chain end predominantly in *racemo* fashion [10,12,13].

Fig. 5 compares the proton NMR spectra of chloride-telechelic PLLA (a) and poly(*t*-butyl acrylate-*b*-L-lactide-*b*-*t*-butyl acrylate) (b) (Experiment 1, Table 1). Peaks at 1.59 and 5.16 ppm were attributed to PLLA main-chain methyl and methine proton resonances, respectively. Peaks at 4.34 and 4.45 ppm represent the methylene protons (EG) of the ethylene glycol initiating moiety and the ultimate methine proton adjacent to the chloride end groups (α^{Cl}), respectively, (Fig. 5(a)). After polymerization of *t*-butyl acrylate, peaks at 1.44 and 2.23 ppm appeared, which were attributed to pendent methyl and main chain methine protons. In addition, the ultimate methine proton, adjacent to the chloride end groups (z'), shifted upfield to 4.14 ppm while main-chain PLLA and ethylene glycol resonances were preserved. The main-chain methylene protons of the poly(*t*-butyl acrylate) segment appeared from 1.24 to 1.68 ppm (convoluted with the main-chain methyl peaks of the PLLA backbone) and from 1.74 to 1.94 ppm. This was attributed to the tacticity described above, where the broad resonances 1.24–1.68 ppm represent the *racemo* and *meso* methylene protons and 1.74–1.94 ppm represent the *meso* methylene protons of the poly(*t*-butyl acrylate) backbone, respectively, [14].

The molar incorporation of *tert*-butyl acrylate was determined by integration of the main-chain methine protons for PLLA at 5.16 ppm (α) and the main-chain methine proton for poly(*tert*-butyl acrylate) at 2.23 ppm (z) (Fig. 5(b)).

SEC-MALLS was used to monitor molecular weight characteristics and molecular weight growth of the chloro-telechelic PLLA macroinitiator and the corresponding triblock copolymers. Fig. 6 shows the shift to lower elution volume upon polymerization of *t*-butyl acrylate indicating an increase in molecular weight.

3.3. Poly(benzyl acrylate-b-L-lactide-b-benzyl acrylate) synthesis and characterization

Benzyl acrylate was also used as a monomer for ATRP from a chloro-telechelic PLLA macroinitiator. Fig. 7 shows the carbon NMR spectra of the PLLA macroinitiator and the resulting benzyl acrylate triblock (Experiment 4, Table 1). Comparison of the spectra shows the disappearance of the terminal methyl (21.7 ppm, β^{Cl}) and methine (52.4 ppm, α^{Cl}) carbons from the chloro-telechelic PLLA (Fig. 7(a)) upon polymerization of benzyl acrylate (Fig. 7(b)). Similar to the *tert*-butyl acrylate system previously described, the absence of these peaks indicates quantitative initiation from the chloride chain end. Likewise, the spectrum in Fig. 7(b) demonstrates retention of main-chain PLLA carbon resonances at 16.8 ppm (methyl, β), 69.1 ppm (methine, α), and

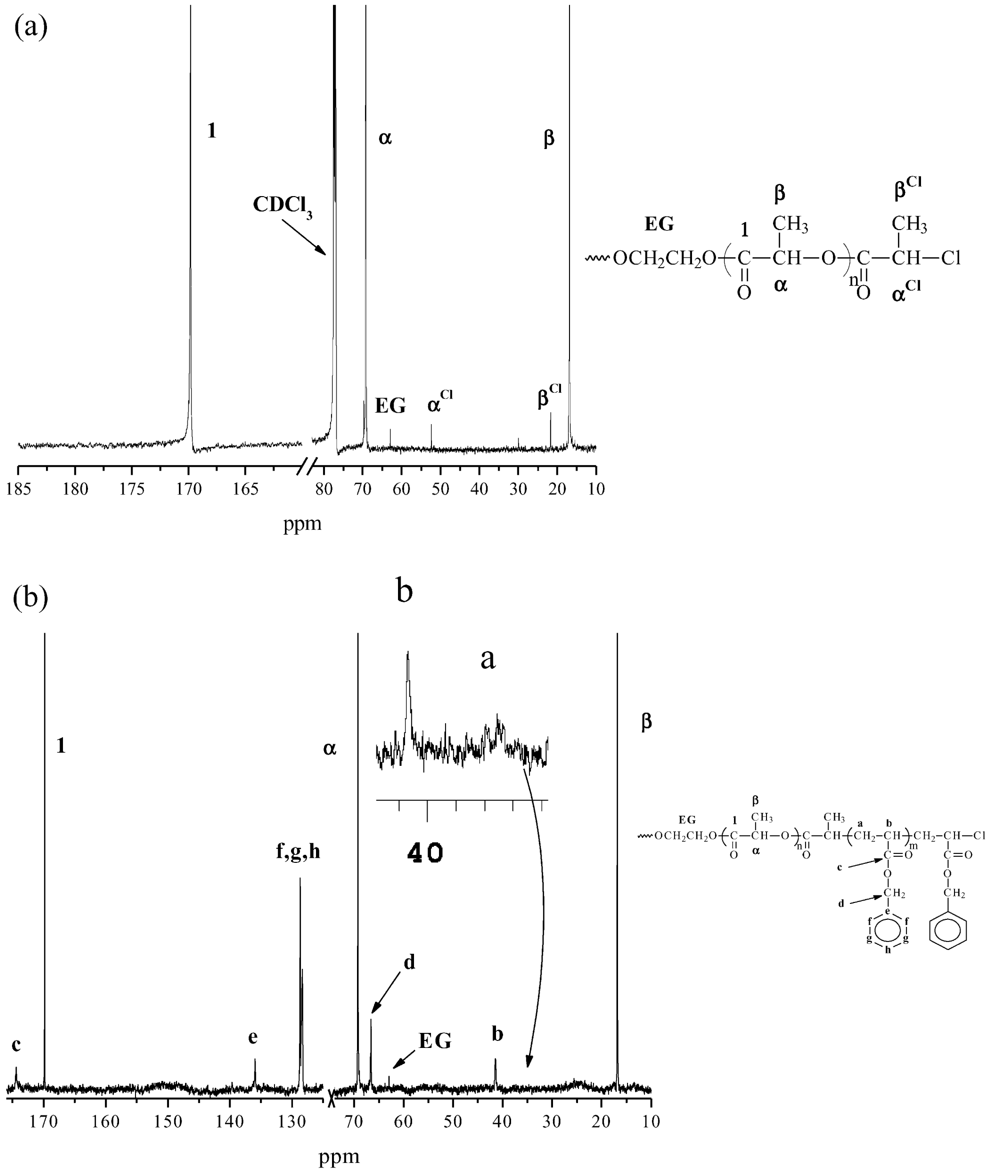


Fig. 7. ^{13}C NMR spectra of chloro-telechelic PLLA (a) and poly(benzyl acrylate-*b*-LLA-*b*-benzyl acrylate) (b) (Experiment 4, Table 2).

169.6 ppm (carbonyl, 1), and the appearance of peaks at 41.5, 136.0 and 174.4 ppm, which were attributed to the main-chain methylene (a), *ipso* aromatic (e), and pendent carbonyl (c) carbon resonances of the benzyl acrylate block, respectively. Again, the peak at 62.9 ppm (ethylene glycol, EG) was visible in both spectra. The structure was further characterized by the appearance of peaks at 35.6 ppm (see insert Fig. 8(b)) and 66.6 ppm attributed to the main chain methylene (a) and pendent methylene/benzyl (d) carbons, respectively. Furthermore, the peak assignment for the main-chain methylene carbon was confirmed using heteronuclear single quantum correlation (2D-hsqc) NMR spectroscopy (data not shown). The remaining aromatic carbons appeared at 128.2–128.5 ppm (f, g) and 136.0 ppm (h).

Additional structural evidence for the incorporation of benzyl acrylate (Fig. 8(b)) onto the chloro-telechelic PLLA (Fig. 8(a)) was obtained using proton NMR spectroscopy. Fig. 8(b) demonstrates the appearance of peaks at 1.3–1.9, 2.2–2.4, 4.9 and 7.3 ppm, which were attributed to the main chain methylene (*p*) and methine (*o*), and pendent methylene/benzyl (*m*), and phenyl (*n*) proton resonances for poly(benzyl acrylate-*b*-LLA-*b*-benzyl acrylate), respectively. Similar to the *t*-butyl acrylate block copolymer (Fig. 5(b)), the main-chain methylene protons (p) were convoluted with the main-chain methyl protons of the PLLA centerblock as a result of tacticity. Retention of peaks at 1.59 ppm (β) and 5.19 ppm (α) indicate the presence of the PLLA centerblock. The ultimate methine proton, adjacent to the chloride end groups, shifted upfield from 4.45 ppm in chloro-telechelic PLLA (α^{Cl}) (Fig. 8(a)) to 4.14 ppm in poly(benzyl acrylate-*b*-LLA-*b*-benzyl acrylate) (o') (Fig. 8(b)).

SEC-MALLS was used to elucidate molecular weights

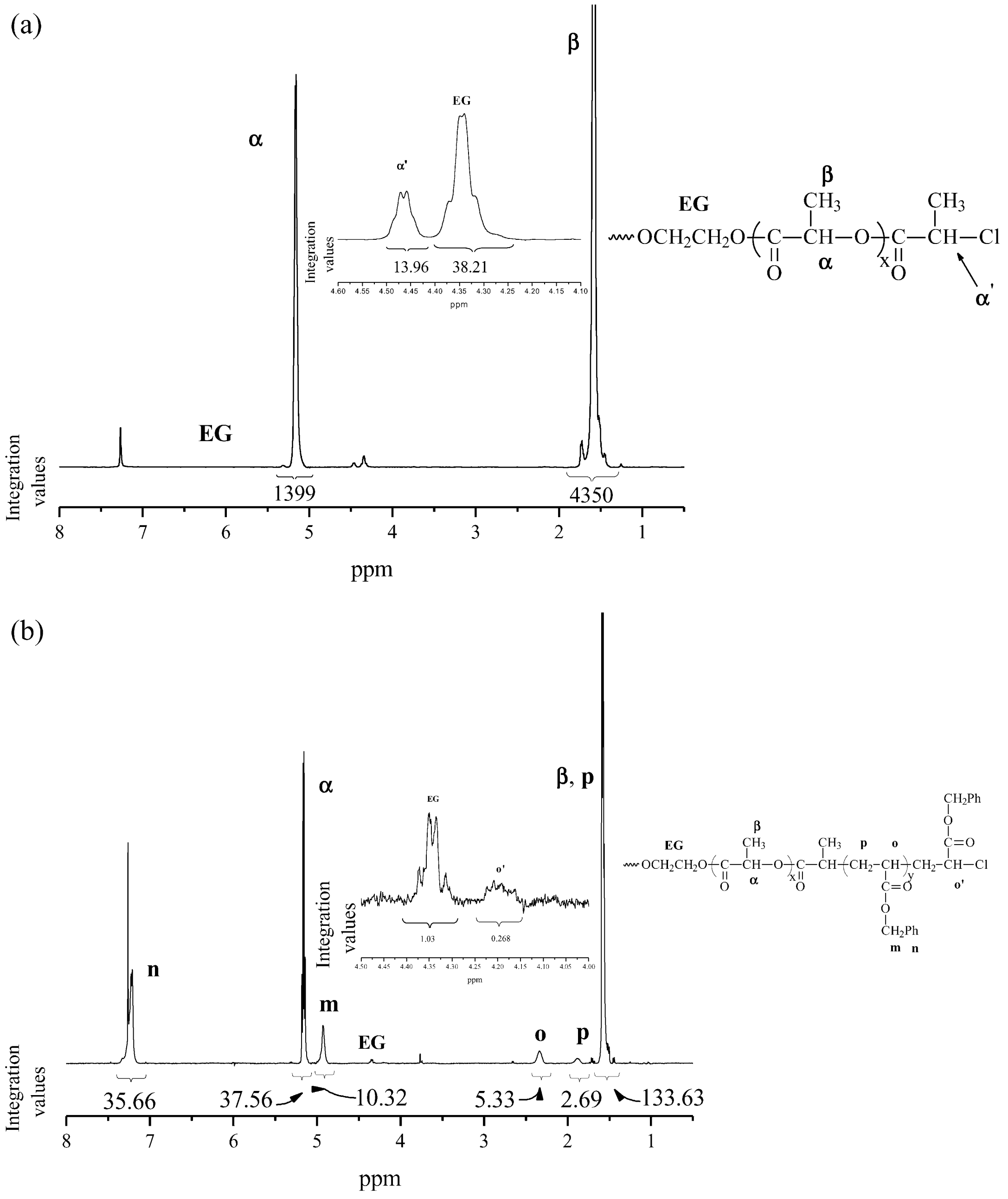


Fig. 8. ^{1}H NMR spectra of chloro-telechelic PLLA (a) and poly(benzyl acrylate-*b*-LLA-*b*-benzyl acrylate) (b) (Experiment 4, Table 2).

and PDIs of the chloride-terminated PLLA macroinitiator and corresponding benzyl acrylate triblock copolymer and to monitor the progress of blocking. Table 2 lists the molecular weight characteristics of the chloro-telechelic PLLA macroinitiator and the corresponding triblock copolymer systems developed after polymerization of both *tert*-butyl acrylate and benzyl acrylate via ATRP.

3.4. Thermal analysis

To determine the glass transition temperature(s) and presence of crystallinity, the triblock copolymers from Experiments 1 and 4 were analyzed using DSC. Fig. 9 compares the T_gs of the hydroxy- (a, 55.7 °C) and chloro-telechelic (b, 59.7 °C) PLLAs with the corresponding *t*-butyl acrylate triblock copolymer (c, 57.2 °C). Each sample, including the triblock material, displays only one T_g. Since the T_gs of the corresponding homopolymers are so close (PLLA, $T_g = 51$ °C; P*t*-BA, $T_g = 46$ °C), DSC was not sensitive enough to resolve the difference between the amorphous phases. PLLA crystallinity was retained after formation of the triblock copolymer, as evidenced by the melting temperature endotherms in trace (c).

The incorporation of poly(*t*-butyl acrylate) effectively disrupted the chain mobility of the PLLA centerblock, which resulted in an increase in the crystallization

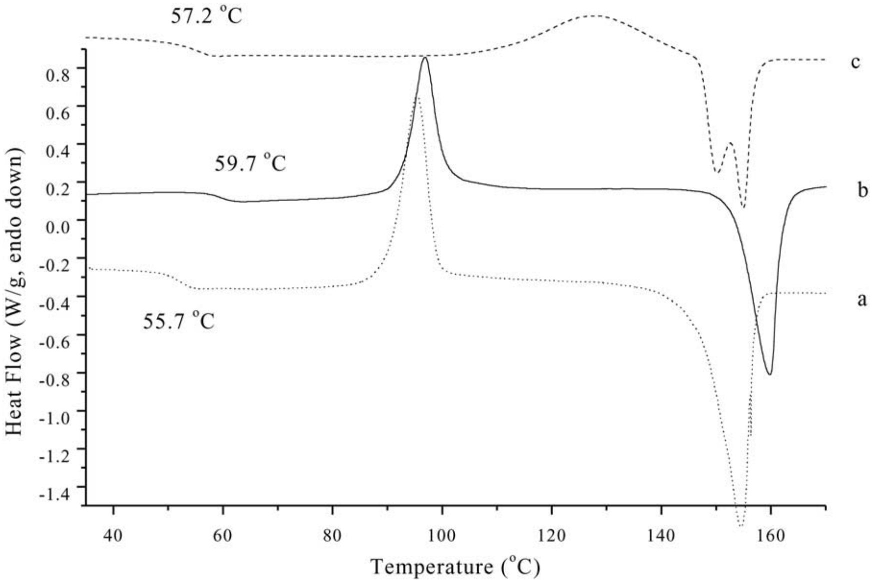


Fig. 9. DSC thermograms for hydroxy-telechelic PLLA (a), chloro-telechelic PLLA (b), and poly(*tert*-butyl acrylate-*b*-LLA-*b*-*tert*-butyl acrylate) (Experiment 1, Table 2) (c).

temperature, T_c, for poly(*t*-butyl acrylate-*b*-L-lactide-*b*-*t*-butyl acrylate) (see Fig. 8(c)). The crystallization exotherm increased because more energy was required in the crystallization process for poly(*t*-butyl acrylate-*b*-L-lactide-*b*-*t*-butyl acrylate) in comparison to both hydroxy- and chloro-telechelic PLLA (traces a and b, respectively).

Poly(benzyl acrylate) homopolymer, on the other hand, displays a T_g of ~5 °C and is sufficiently distinguished from the PLLA block. This is shown in Fig. 10 where two T_gs are observed: one at 5 °C for the benzyl acrylate block and one at 42 °C for the PLLA block. The observance of two T_gs is consistent with block copolymers having immiscible amorphous domains [15–18].

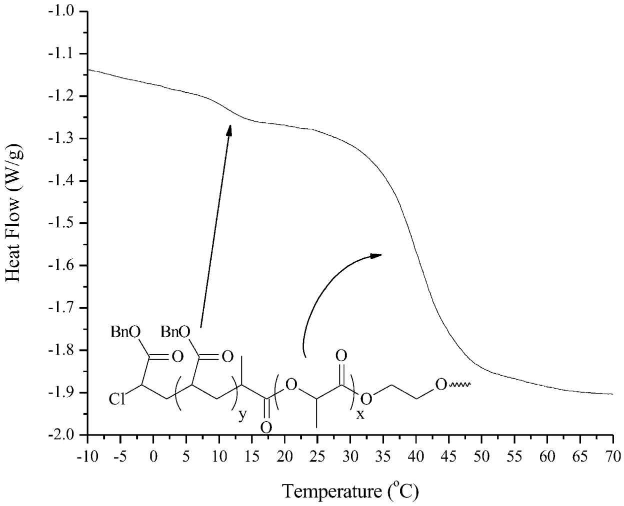


Fig. 10. DSC thermogram illustrating dual T_gs for poly(benzyl acrylate-*b*-LLA-*b*-benzyl acrylate) at 6 and 42 °C, attributed to the benzyl acrylate and LLA blocks, respectively. (Experiment 4, Table 2).

4. Conclusions

The transformation of hydroxy-telechelic PLLA to chloro-telechelic PLLA using thionyl chloride/pyridine has been reported. ^1H and ^{13}C NMR spectroscopies and SEC-MALLS have been used to confirm the structure and molecular weight characteristics of the PLLAs. The chloro-telechelic PLLA was subsequently used as a macroinitiator for the polymerization of both *tert*-butyl acrylate and benzyl acrylate using ATRP. This is the first report of ATRP initiated from chloride-terminated PLLA. DSC revealed two T_gs for poly(BnA-*b*-LLA-*b*-BnA), characteristic of block copolymers with incompatible amorphous domains. Only one T_g was observed for poly(*t*-BA-*b*-LLA-*b*-*t*-BA) presumably because the thermal transitions of the homopolymers were too close to one another. PLLA crystallinity was observed in each acrylate based system providing additional evidence for block copolymer architecture. In all cases, the actual incorporation of acrylate into the triblock copolymer was lower than the molar feed ratio as the copolymer became increasingly less soluble upon conversion of acrylate. *tert*-Butyl acrylate and benzyl acrylate were chosen for potential ease of conversion to pendent carboxylic acid moieties in the presence of the chemically and thermally sensitive PLLA backbone. This, in turn, could lead to a new class of poly(ester-acrylates) containing degradable segments.

This novel combination of ring-opening (ROP) and atom transfer radical polymerization (ATRP) techniques creates numerous possibilities for block copolymer architectures. Simply choosing the appropriate initiator fragment in the initial ROP step facilitates the design of linear, telechelic and star polylactides (e.g., poly(*rac*-LA), poly(D-lactide), and PLLA), which can subsequently be employed as macroinitiators after their conversion to terminal halides (e.g., chloride or bromide). The wide choice of acrylate monomers amendable to ATRP represents a distinct advantage of the method. Enhanced cross-over kinetics, leading to more uniform PDIs can possibly be accomplished through the use of a terminal bromide group on the PLLA macroinitiator.

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