Synthesis and Characterization of AB-type Copolymers Poly(L-lactide)-*block*-poly(methyl methacrylate) via a Convenient Route Combining ROP and ATRP from a Dual Initiator

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ABSTRACT: Diblock copolymers of poly(L-lactide)-*block*-poly(methyl methacrylate) (PLLA-*b*-PMMA) were synthesized through a sequential two-step strategy, which combines ring-opening polymerization (ROP) and atom transfer radical polymerization (ATRP), using a bifunctional initiator, 2,2,2-trichloroethanol. The trichloro-terminated poly(L-lactide) (PLLA-Cl) with high molecular weight ($M_{n,GPC}$ = 1–12 × 10^4 g/mol) was presynthesized through bulk ROP of L-lactide (L-LA), initiated by the hydroxyl group of the double-headed initiator, with tin(II) octoate ($Sn(Oct)_2$) as catalyst. The second segment of the block copolymer was synthesized by the ATRP of methyl methacrylate (MMA), with PLLA-Cl as macroinitiator and CuCl/*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) as catalyst, and dimethyl sulfoxide (DMSO) was chosen as reaction medium due to the poor solubility of the macroinitiator in conventional solvents at the reaction temperature. The trichloroethoxyl terminal group of the macroinitiator was confirmed by Fourier transform infrared spectroscopy (FTIR) and ^{1}H-NMR spectroscopy. The comprehensive results from GPC, FTIR, ^{1}H-NMR analysis indicate that diblock copolymers PLLA-*b*-PMMA ($M_{n,GPC}$ = 5–13 × 10^4 g/mol) with desired molecular composition were obtained by changing the molar ratio of monomer/initiator. DSC, XRD, and TG analyses establish that the crystallization of copolymers is inhibited with the introduction of PMMA segment, which will be beneficial to ameliorating the brittleness, and furthermore, to improving the thermal performance. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 2379–2388, 2010

Key words: dual initiator; polylactide; poly(methyl methacrylate); diblock copolymer; ATRP

INTRODUCTION

Poly(lactide) (PLA), due to its good mechanical properties, biocompatibility, biodegradability, and bioresorbability, has been explored for wide applications, including in *vivo* degradable/resorbable medical implants and sutures, and in medicine and pharmacy as controlled drug delivery materials.[1–4] Based on its biodegradability and ecosystem-friendly properties,[5,6] PLA can also be an ideal replacement of nondegradable polymers in numerous applications, such as yard waste bags, food containers, agricultural mulch films, etc. Recent technological developments have made PLA products economically competitive with petroleum-derived plastics.[7]

However, PLA homopolymer is usually brittle and lacks flexibility on account of its crystallinity, in addition, its degradation rate is uncontrollable, which hardly meet the requirements preferably not only for general materials applications but also for medical materials applications, for example, polymer-based controlled-release drug delivery systems for different drugs require that carrier materials should have different degradation rates, and the need for higher mechanical strength is essential for bone-repairing materials. For the sake of improving its mechanical properties as well as the controlled degradation, PLA can be modified by copolymerization, blending, and other methods,[8,9] nevertheless, it still cannot be used to manufacture low-cost products as general plastic materials. In recent years, though researches on modifying PLA by copolymerizing have been widely reported,[10–16] those reports are mainly concerned with improving the hydrophilicity and achieving self-assembly properties, which may have great potential use in controlled drug-release systems, etc. The principal synthesis strategy is usually using preprepared hydroxy-terminated macroinitiator to initiate the ring-opening polymerization (ROP) of lactide[10,11,15] or adopting the chain extensions of PLLA with difunctional

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compounds,[12,13] while copolymerizable monomers are limited by using this strategy in that the polymerization of hydroxy-terminated macroinitiator from vinyl monomer is tedious.

As is well-known, atom transfer radical polymerization (ATRP) which was first reported by Matyjaszewski[17] and Sawamoto[18] is an important "living"/controlled radical polymerization (CRP) to be used or used as the main polymerization method to synthesize a wide variety of polymers with special structure and multicomponent copolymers with special performance including block copolymers, graft copolymers, random copolymers, gradient copolymers, star polymers, hyperbranched polymers, and functional polymers, etc.[19] One technique has been developed combining ROP and ATRP to synthesize various well-defined copolymers, such as di/triblock copolymers,[20–25] star-shaped copolymers,[26–29] comb-shaped copolymers,[30] etc. Most of these examples are about ROP of lactones and ATRP of acrylic esters,[20,22,24,25] and the conventional strategy is that hydroxyl-terminated polylactones are prepared firstly via ROP of lactones, and sequentially converted into halogen-terminated ATRP macroinitiators through an intermediate transformation step, and then are used to initiate ATRP of acrylic esters.[22,24,25] Nevertheless, the ATRP macroinitiator obtained by means of intermediate conversion steps needs to be prior purified before being used in the ATRP step,[31] thus a more effective method has been more widely employed in the preparation of block copolymers, which is based on a bifunctional initiator containing two functional groups capable of initiating two polymerizations occurring by different mechanisms without intermediate conversion steps,[32] e.g. multifunctional initiators synthesized purposively were utilized to combine ROP and ATRP, resulting in various copolymers with various structures and composition.[20,21,24] In spite of that, multifunctional initiators usually need to be synthesized designedly, and the process of which is somewhat cumbersome because very few industrial reagent could be eligible to be used as multifunctional initiator. Hawker[33] has successfully made use of 2,2,2-tribromoethanol as a novel bifunctional initiator to synthesize diblock copolymer PCL-*b*-PMMA by combining ROP of ε-caprolactone and ATRP of MMA through either the 'caprolactone polymerization first followed by polymerization of methyl methacrylate' approach or the reverse strategy. Ke Sha[34,35] has reported the application of 2,2,2-trichloroethanol (TCE) as bifunctional initiator leading to the synthesis of AB-type diblock copolymer PCL-*b*-PSt by the integration technique of ROP and ATRP. Nonetheless, it is not yet reported that TCE is applied to initiate the ROP of lactide to synthesize trichloro-terminated polylactide, which can be used as macroinitiator for ATRP of MMA resulting in diblock copolymer PLLA-*b*-PMMA with the intention of improving properties of PLLA.

By combining ring-opening polymerization (ROP) of L-Lactide (L-LA) and followed atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA), in this article, two-step synthesis of AB-type copolymer poly(L-lactide)-*block*-poly(methyl methacrylate) (PLLA-*b*-PMMA) was carried out to construct designed diblock molecular architecture, and hence to inhibite the crystallinity of PLLA. An easily acquiring novel bifunctional initiator, 2,2,2-trichloroethanol, which can not only initiate the ring-opening polymerization of L-lactide, but also give the resulting high-molecule-weight polylactide with single trichloroethyl terminal groups (PLLA-Cl) without the need for intermediate functionalization steps, was used in the synthesis of PLLA. Then the trichloro-terminated PLLA-Cl was further used as a macroinitiator in the second step, namely the ATRP of MMA in polar solvent (DMSO), which may provide a certain foundation for the application of using high molecular weight PLLA as macroinitiator, because it is difficult to dissolve in nonpolar solvents. Studies in this article may provide a way to prepare block copolymers using PLLA as macroinitiator. Furthermore, the properties of PLLA could be improved by copolymerizing. All of these will extend some idea to develop PLLA as a commodity polymer for the replacement of nondegradable polymers in manufacturing low-cost products.

EXPERIMENTAL SECTION

Materials

L-Lactide (*L*-LA) (≥99%) from Beijing Yuan-shengrong Technology Co. was purified by recrystallizing with ethyl acetate and dried under vacuum at 35°C. Methyl methacrylate (MMA) (AR, Shanghai Jingchun Chemical Reagent Co., China) was purified by extracting with 5% sodium hydroxide aqueous solution, followed by washing with deionized water and dried with anhydrous magnesium sulfate overnight, and finally distillated under vacuum at 40°C and stored at −5°C. *N*,*N*,*N*′,*N*″,*N*″-Pentamethyldiethylenetriamine (PMDETA) (≥99%, Sigma–Aldrich), stannous octanoate ($Sn(Oct)_2$) (≥95%, Sigma–Aldrich), and 2,2,2-trichloroethanol (≥99%, Shanghai Jingchun Chemical Reagent Co., China) were all used without further purification. CuCl (≥97%) purchased from Shanghai Yinyuan Chemical Reagent Factory (China) was purified by washing with glacial acetic acid till the liquid being colorless followed by methanol in a Schlenk tube under a argon atmosphere, and dried at 80°C under the argon flow. Dimethyl sulfoxide (DMSO) (GR, Shanghai Jingchun Chemical

Reagent Co., China) was purified through drying with CaH_2 and the decompressed distillation. Tetrahydrofuran (THF) (AR; Chengdu Kelong Chemical Reagent Factory, China), ethanol (AR; Shanghai Organic Chemical Engineering Reagent Institute, China), and chloroform (AR; Chengdu Kelong Chemical Reagent Factory, China) were all used without further purification.

Analysis and measurements

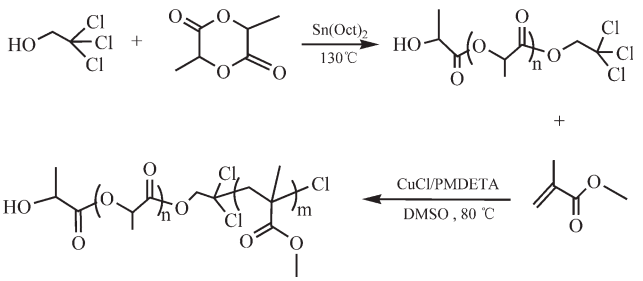
The number-average molecular weight (M_n) and molecular-weight dispersity ($Đ_M = M_w/M_n$) of the obtained polymers were measured by gel permeation chromatography (GPC) analysis on a Agilent 1100 series liquid chromatograph equipped with a refractive index detector (G 1362 A) and a series of 10^4 and 100 Å pore sizes polydivinylbenzene columns thermostated at 35°C. Tetrahydrofuran was used as the mobile phase at a flow rate of 1.0 mL/min, and the column calibration was performed with polystyrene standards.

Approximately 20 mg of vacuum-dried sample was dissolved with 1 mL chloroform, and then suitable amount of the solution was coated on the potassium bromide (KBr) plates, which was dried by infrared heat lamp to produce pellets for analysis and Fourier transform infrared (FTIR) spectra were recorded with an accumulation of 64 scans over the wavenumber range of 400–4000 cm^{-1} and a resolution of 0.5 cm^{-1} on a Fourier transform infrared spectrometer Nicolet 560 system.

^{1}H-NMR spectra were obtained with a Brucker ARX400 spectrometer at 600 MHz under ambient temperature, using chloroform-*d* and tetramethylsilane (TMS) as the corresponding solvent and internal chemical shift standard, respectively. Based on the number-averaged molecular weight (M_n) of PLLA determined from the GPC results, the molecular weight of the PMMA segment was determined using a ^{1}H-NMR spectrum by examining the ratio of methine protons in the PMMA segment and methylene protons in the PLLA segment.

Differential scanning calorimetry (DSC) thermograms were conducted using a Mettler Toledo DSC 1 STAR system. Experiments were carried out with 5–8 mg samples, under a heating rate of 10°C/min, in a sealed aluminum pan under nitrogen purge. The first heating scan was from 0°C to 210°C, and the samples were first kept at 210°C for 5 min to eliminate the thermal history, and then cooled to 0°C at a cooling rate of 10°C/min. Finally, after being kept at 0°C for 5 min, the samples were again heated to 210°C at the same heating rate. The glass transition temperatures (T_g) was defined as the midpoint of the transition from the second heating scan.

Thermogravimetric analysis (TGA) was performed with a TA instrument SDT Q600 thermogravimetric analyzer in the range of ambient temperature to 450°C at a heating rate of 10°C/min, under steady flow of nitrogen at 100 mL/min.



Scheme 1 Synthesis strategy for PLLA-*b*-PMMA diblock copolymers.

The X-ray diffractometric (XRD) analysis was carried out on a Philips X'Pert Pro MPD diffractometer equipped with a Cu Kα (λ = 154 nm) source operated at 40 KV and 40 mA, adopting continuous scanning. The scan step size and the scanning velocity were set as 0.03°, 9°/min, separately. The diffraction intensity was measured by monitoring the diffraction angle 2θ from 3 to 60 degree.

Polymerization

Synthesis of the trichloromethyl terminated PLLA via bulk ROP

The preparation of the macroinitiator PLLA-Cl was carried out by ROP using TCE as initiator (Scheme 1). In a typical polymerization, the L-lactide (5 g, 0.035 mol) was combined with 2,2,2-trichloroethanol (0.05 g, 0.35 mmol) in a flame-dried tailor-made flask under argon and the flask was evacuated and backfilled with argon three times. Tin(II) octoate ($Sn(Oct)_2$) (7 mg, 0.017 mmol) was dissolved in 0.3 mL dry tetrahydrofuran and then added in the mixture. The flask, sealed under vacuum, was immersed in an oil bath at 130°C. The melt solution was stirred for 5 h, turning into solid state gradually, and then the flask was removed from the oil bath, cooled to room temperature. The polymer was dissolved with 20 mL chloroform for the precipitation into 500 mL ice cold ethanol, and then was centrifuged. The solid was collected and dried in *vacuo* oven at 35°C for 48 h. IR [KBr, cm^{-1}, L-LA]: 2996 (ν_{C-H}), 2932 (ν_{C-H}), 1761 ($\nu_{C=O}$), 1450 (δ_{C-H}), 1356 (δ_{C-H}), 1273 (ν_{C-O-C}), 1095 (ν_{C-O-C}), 650, 934 ($\nu_{ring\ skeleton}$). IR [KBr, cm^{-1}, PLLA-Cl]: 2998 (ν_{C-H}), 2947 (ν_{C-H}), 1756 ($\nu_{C=O}$), 1453 (δ_{C-H}), 1482 (δ_{C-H}), 1361 (δ_{C-H}), 1265 (ν_{C-O-C}), 1186 (ν_{C-O-C}), 1131 (ν_{C-O-C}), 1092 (ν_{C-O-C}), 810 (ν_{C-Cl}), 871 (amorphous polylactide characteristic absorption), 757 (crystalline polylactide characteristic absorption). ^{1}H-NMR [$CDCl_3$, 600 MHz], δ [ppm]: 5.14–5.19, (q, 1H, OC*H*CH_3CO); 1.57, 1.59, (d, 3H, OCHC*H*$_3$CO); 1.49, 1.50, (d, 3H, HO(C*H*$_3$)CH—); 4.3–4.4, (q, 1H, HO(C*H*)CH_3—); 4.9, (d, 2H, Cl_3CH_2O—).

Synthesis of the diblock copolymers PLLA-*b*-PMMA from the macroinitiator via ATRP in DMSO

The diblock copolymer PLLA-*b*-PMMA was prepared via further ATRP polymerization of MMA with CuCl/PMDETA as catalyst system and PLLA-Cl as macroinitiator (Scheme 1). Typically CuCl (6 mg, 0.06 mmol) and PLLA-Cl (0.5 g) were added to a tailor-made flask and the system was cycled between vacuum and argon three times to remove the oxygen. Then degassed PMDETA (10 mg, 0.06 mmol), monomer (1 g, 10 mmol), and DMSO (4 mL) were added using degassed syringes. The solution was further deoxygenated by three freeze-pump-thaw cycles and the flask was placed in an oil bath held by a thermostat at 80°C for 10 h. After cooling, the reaction mixture was diluted with chloroform, passed through a neutral alumina column to remove the catalyst and then isolated by precipitation in methanol, followed by drying in vacuum. IR [KBr, cm^{-1}]: 2998, 2947 (ν_{C-H}, in PLLA and PMMA), 1756 ($\nu_{C=O}$, in PLLA), 1731 ($\nu_{C=O}$, in PMMA), 1483 (δ_{C-H}, in PMMA), 1452, 1384 (δ_{C-H}, in PLLA and PMMA), 1359 (δ_{C-H}, in PLLA), 1271, 1188 (ν_{C-O-C}, in PLLA and PMMA), 1242, 1148 (ν_{C-O-C}, in PMMA), 1092 (ν_{C-O-C}, in PLLA), 867 (amorphous characteristic absorption), 757 (crystalline characteristic absorption). ^{1}H-NMR [$CDCl_3$, 600 MHz], δ [ppm]: 5.14–5.19 (q, C*H*CH_3, PLLA segment); 1.57, 1.59 (d, —CH_3, PLLA segment); 3.60 (s, —OCH_3, PMMA segment); 1.73–2.07 (m, —CH_2—, PMMA segment); 0.85, 1.02 (s, CH_3—C—, PMMA segment)

RESULTS AND DISCUSSION

Synthesis of trichloromethyl terminated PLLA via bulk ROP

In general, two main methods are exploited to synthesize polylactide, and one of those is the direct condensation polymerization of lactic acid, which cannot give high molecular weight commonly.[36] Afterwards, the ring-opening polymerization of lactide is most applied to obtain high molecular weight polylactide.[36] Various reaction mechanisms for the ring-opening polymerization of lactide have been reported, such as the coordination insertion, anionic, cationic mechanisms, etc., and it is considered that different catalysts lead to different reaction mechanisms.[36] Stannous octoate was chosen as a catalyst in our study because of its high catalytic efficiency and the safety for human, which has accredited by FDA.[37] Generally, trace hydroxy compounds are considered to be initiators for the ring-opening polymerization of lactide.[38] Therefore, some compounds with hydroxy groups can be selected artificially as initiator for the ring-opening polymerization of lactide, and it is generally believed that this would make the reaction rate faster than that without any hydroxy compounds added deliberately. Furthermore, it is very necessary to dry the reagents (especially the lactide) thoroughly to minimize the possibility of competitive initiation between water and initiator, in that the former is also an effective initiator for ROP.

A series of $RCCl_3$-type initiators,[39,40] including 2,2,2-trichloroethanol, has been applied as initiators of the ATRP of MMA. What interest us is that 2,2,2-trichloroethanol (TCE),[34,35] titanium alkoxide containing halogen groups synthesized through the ester-exchange reaction of titanium *n*-propoxide and 2,2,2-trichloroethanol,[41] as well as 2,2,2-tribromoethanol (TBE),[33] have been used as dual initiators for the ROP of lactones and the ATRP of vinyl monomers to synthesize diblock copolymers PCL-*b*-PMMA/ PCL-*b*-PSt/ PCL-*b*-PBA without intermediate transformation steps.

TCE contains a single primary alcohol terminated group, which can initiate ROP and an activated trichloromethyl group, the effective initiating group for ATRP, in the other chain end, and consequently needs no synthesis step. Thus, TCE was chosen to prepare the trichloro-terminated polylactide (PLLA-Cl) by ROP of L-LA using $Sn(Oct)_2$ as catalyst, which was subsequently used as macroinitiator to induce the ATRP of MMA to yield the diblock copolymers PLLA-*b*-PMMA, aiming at reducing the crystallinity and degradation rate of PLLA to improve the toughness and weatherability.

TCE has not been applied to initiate the ROP of lactide to date, so the end structure of PLLA-Cl must be validated first, whereas it could not be directly confirmed by any means because of its high molecular weight. Thus, to determine the existence of the end structure of trichloromethyl terminated

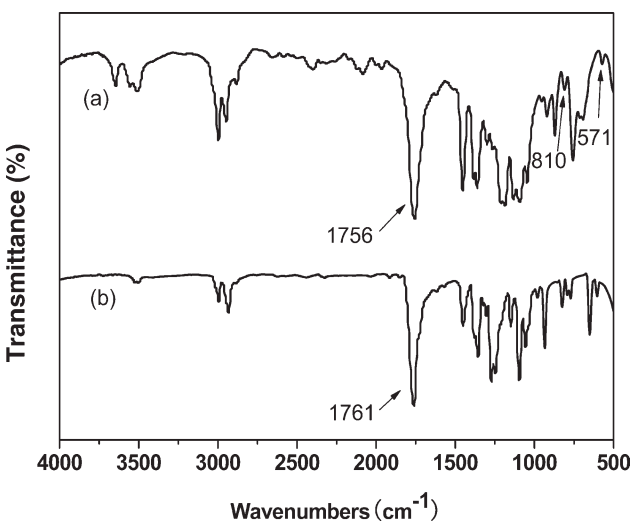


Figure 1 FTIR spectra of (a) macroinitiator PLLA-Cl and (b) L-LA.

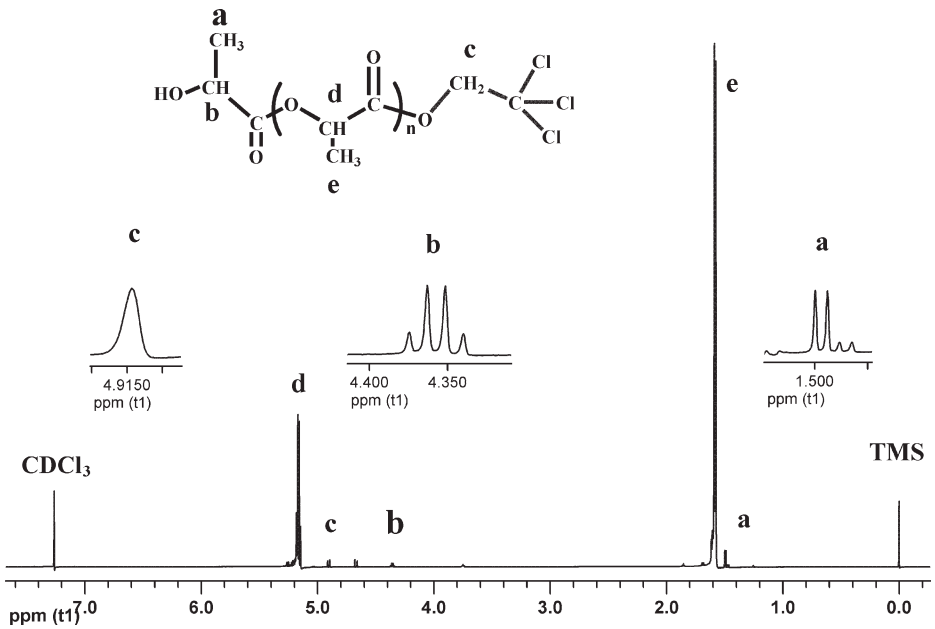


Figure 2 ^{1}H-NMR spectrum for PLLA-Cl.

PLLA, an oligo(L-lactide) was synthesized through a model reaction using a similar procedure as for polymerization under the following conditions: $[Sn(Oct)_2]/[TCE]/[L\text{-lactide}] = 0.025/1/20$ at 130°C for 3 h. The end structure of the obtained PLLA-Cl was confirmed by FTIR and ^{1}H-NMR. As shown in Figure 1(**a**), the weak absorption peaks at 3645, 810 cm^{-1} are interpreted as the hydroxyl and trichloromethyl groups at one end of polylactide and the other. The corroboration is from ^{1}H-NMR, and Figure 2 shows minor resonances chemical at 4.3–4.4 ppm and 4.9 ppm, which can be attributed to the methyl protons attached to terminal hydroxyl group and the methylene protons attached to trichloromethyl (—CCl_3) from the initiator at the other end of the macroinitiator, respectively. The cross-checked analysis by FTIR and ^{1}H-NMR spectra corroborates that the initiator TCE has been successfully attached to PLLA chains.

The molecular weight of PLLA ($M_{n,GPC}$, 5400 g/mol) determined by GPC is higher in comparison with that based on the integration values of the peaks in ^{1}H-NMR ($M_{n,NMR}$, 3800 g/mol) and that calculated by a correction factor 0.58 ($M_{n,calib}$, 3100 g/mol),[42] while the latter couple are close to each other. The molecular weight obtained by GPC depends on the hydrodynamic volume, so it is relative and should be calibrated with the homologous narrow-distribution polymer standard absolute molecular weight determined by static light scattering (SLS) or other methods. Thus, the most likely cause of the discrepancy was thought to lie in the GPC analysis, which was calibrated using polystyrene standards. Nevertheless, it is clear that the experimental results are much greater than the theoretically predicted value ($M_{n,theo}$, 3000 g/mol), which could be attributed to the low efficiency of initiator

TABLE I
Molecular Weight Characteristics of Macroinitiators Prepared by Ring-opening Polymerization Using Trichloroethanol as Initiator

Macroinitiator	$[M]/[I]$ (mol/mol)	Conversion (%)	$M_{n,GPC}$[a]	$M_{n,calib}$[b]	$M_{n,theo}$[c]	$Đ_M$ ($M_{w,GPC}/M_{n,GPC}$)
I1	500 : 1	95.6	120,000	69,600	69,000	1.70
I2	100 : 1	95.3	34,100	19,700	13,900	1.37
I3	50 : 1	95.1	14,300	8200	7000	1.26
I4	100 : 1	95.3	38,000	22,000	13,900	1.37
I5	20 : 1	95.1	5400	3100	3000	1.36

[a] $M_{n,GPC}$ obtained by GPC.
[b] $M_{n,calib} = M_{n,GPC} \times 0.58$.[42]
[c] $M_{n,theo} = M_w$ of initiator + ($[M]/[I] \times 144$ (molecular weight of the monomer) × conversion).

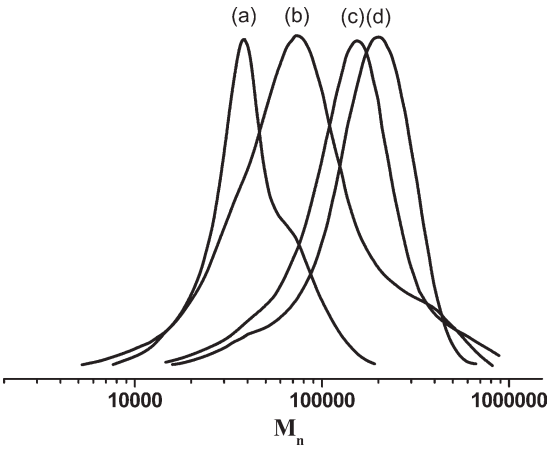


Figure 3 Comparison of GPC traces for (a) the PLLA-Cl macroinitiator, **I2**, and (b)–(d) the block copolymers obtained by ATRP with different MMA content (Table II) in DMSO at 80°C (b) **B1,** (c) **B2,** (d) **B3**.

on account of the partially loss of TCE in the experiment process and the volatilization of TCE at experiment temperature 130°C though the reasons may be manifold. GPC data of PLLA with different monomer/initiator ratio are shown in Table I, indicating that monomer/initiator ratio can be a good control means of polymer molecular weight. It is believed that the existence of weak shoulder peak on the curve in Figure 3 is attributed to the farthing residual water in the reaction system, which can also initiate ring-opening polymerization of the L-lactide at a different reaction rate comparing with 2,2,2-trichloroethanol. In addition, the $Sn(Oct)_2$-promoted ring-opening polymerization is known to be accompanied by side reactions like inter- and intra-molecular transesterification, as $Sn(Oct)_2$ also acts as a transesterification catalyst when approaching the polymer/monomer equilibrium, which contribute to the ratherish broad molecular weight dispersity ($Đ_M$) of macroinitiators. It's also probable that the broadening of the molecular weight of PLLA could result from the lack of control in the polymerization arising out of the low efficiency of TCE. With increasing the monomer/initiator ratio, the $Đ_M$ of the macroinitiators decreases obviously as shown in Table I, in that the influence of other hydroxy compounds in the system is weakened.

Synthesis of the diblock copolymers PLLA-*b*-PMMA from the macroinitiator via ATRP in DMSO

High molecular weight macroinitiators synthesized according to the aforementioned methods were difficult to dissolve in the nonpolar solvents, e.g. toluene,[20,30] which are usually used as solvent in ATRP, and therefore a strong polar solvent dimethyl sulfoxide (DMSO), which is also a viable solvent for the ATRP of MMA and can play a crucial role on the enhancement of the rate of polymerization,[43] was chosen as reaction medium for the ATRP of MMA, using trichloro-terminated polylactide as the initiator.

As for "living"/controlled radical polymerization, it is required that living species (growing radicals) are in a fast dynamic equilibrium with the dormant species, which induces a lower stationary concentration of living species. Many factors will affect this dynamic equilibrium, further influencing the controllability of the polymerization, one of which is the polarity of the solvent.[43] As DMSO, which may have an influence on the polymerization due to its affinity with Cu(II), and competitive coordination of oxygen atoms of DMSO at the metal,[43] was used as solvent in the ATRP of MMA, PMDETA with a relatively strong complexation activity for metal ions was chosen to lower the impact of the solvent polarity on the polymerization.

The trichloro-terminated polylactide was used to initiate the polymerization of methyl methacrylate to give a block copolymer with no intermediate steps. As shown in Figure 3, the molecular weight of the block copolymer increases in a systematic way associating with increasing amounts of methyl methacrylate with little evidence of unreacted starting

TABLE II
ATRP of MMA with CuCl/PMDETA Catalyst System, Initiated by PLLA-Cl macroinitiators (I2, $M_{n,\text{calib}}$ = 19,700, $Đ_M$ = 1.37; I4, $M_{n,\text{calib}}$ = 22,000, $Đ_M$ = 1.37) in DMSO at 80°C; [PLLA-Cl]/[CuCl]/[PMDETA] = 1 : 1 : 2.5

PLLA-*b*-PMMA	PLLA-Cl	[MMA]/[PLLA-Cl]	Reaction time (h)	Monomer conversion	$M_{n,\text{GPC}}$ ($\times 10^{-4}$)	$Đ_M$
B1	**I2**	500 : 1	24	67.2	5.68	1.92
B2	**I2**	1000 : 1	24	68.2	11.10	1.60
B3	**I2**	2000 : 1	24	51.5	13.40	1.44
B4	**I4**	2000 : 1	24	39.1	10.93	1.40
B5	**I4**	2000 : 1	48	39.9	9.65	1.56
B6	**I4**	2000 : 1	72	50.1	12.31	1.88

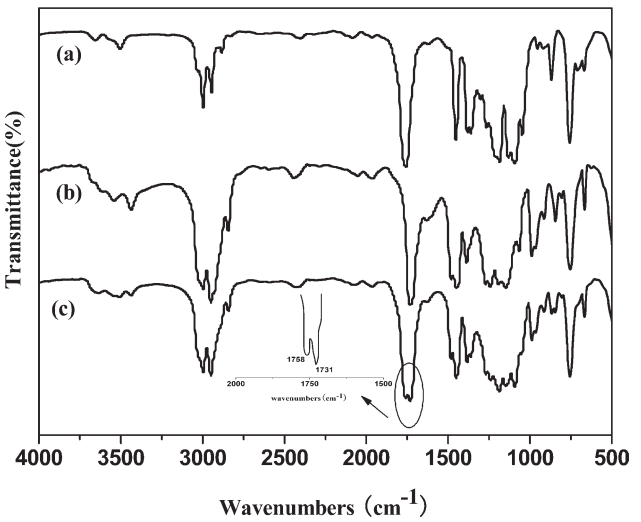


Figure 4 FTIR spectra of (a) PLLA-Cl, **I2,** (b) PMMA, **M2**, and (c) copolymer, **B1**.

material. It is obviously that the molecular weight dispersity ($Đ_M$) of the block copolymers is appreciably broad, which can be mainly attributed to the broadening of the molecular weight of PLLA. Moreover, the introduction of moisture during the removal of aliquot still cannot be totally precluded. In addition, the molecular weight dispersity ($Đ_M$) of copolymers shows a lowering tendency as the content of methyl methacrylate increases, gradually approaching to that of the macroinitiator, as shown in Figure 3, which is consistent with results reported before.[44] For instance, the block copolymer, **B3**, has a number average molecular weight of 13.40×10^{-4} and $Đ_M$ of 1.44, and the corresponding macroinitiator, **I2**, has a molecular weight of 1.97×10^{-4} and $Đ_M$ of 1.37. It should also be noted that, the molecular weight dispersity of the copolymers increased with increasing the reaction time, as can be seen from Table II, which probably because the possible side reactions, e.g., termination between radicals, can not be negligible with prolonging reaction time. Besides, this can be attributed to that the other two chlorine atoms at the end of the macroinitiator may also initiate the ATRP process.

The FTIR spectrum of diblock copolymer, together with macroinitiator PLLA-Cl and PMMA, is shown in Figure 4. The double peaks appear at 1758, 1731 cm^{-1} on the curve of IR absorbance of diblock copolymer [Fig. 4(c)], which are characteristic of carbonyl C=O stretching in polylactide and poly (methyl methacrylate) chain segments, severally. This along with other characteristic vibrational bands due to polylactide and poly(methyl methacrylate) confirms the presence of both the two segments structure in the diblock copolymer.

The structure of the block copolymer is further confirmed by ^{1}H-NMR (Fig. 5), revealing resonances correlating to both the polylactide and poly(methyl methacrylate) blocks while GPC analysis (Fig. 3 and Table II) shows the expected increase in molecular weights and infrared spectra (Fig. 4) show absorption bands from the two segments above. Comparing the integrated intensities for the peaks **a** (1H, OC*H*CH_3CO, in PLLA segment) and **c** (3H, —OCH_3, in PMMA segment) to calculate the molar ratio of the two blocks as 1 : 1.16, the number average

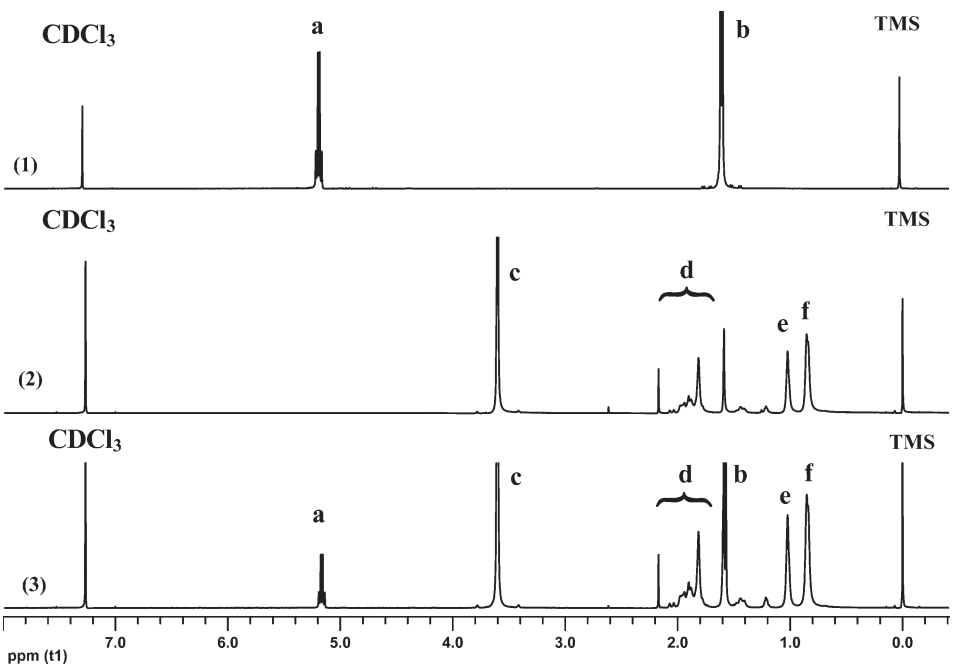


Figure 5 Comparison of ^{1}H-NMR spectra for (1) PLLA-Cl, **I2**, (2) PMMA, **M2**, and (3) copolymer, **B1**.

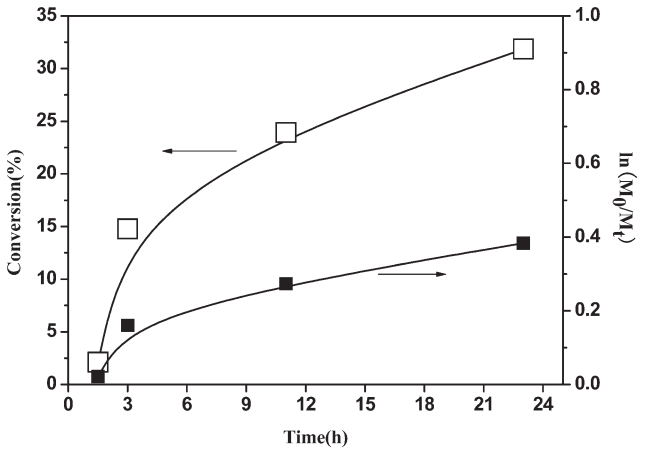


Figure 6 Plots of monomer conversion vs reaction time and ln (M_0/M_t) vs reaction time for the ATRP of MMA in DMSO at 80°C.

molecular weight ($M_{n,\mathrm{NMR}}$) of the block copolymer (**B1**) can be calculated to be 4.71×10^4 g/mol based on the starting polylactide (**I2**) with $M_{n,\mathrm{calib}}$ being 1.97×10^{-4} g/mol, which is in close agreement with $M_{n,\mathrm{theo}}$ (5.33×10^4 g/mol) calculated on the basis of the monomer conversion and $M_{n,\mathrm{GPC}}$ (5.68×10^4 g/mol) from GPC. Significantly, resonances of the CH_3—C— in PMMA blocks reveal twin peaks **e** and **f**, which are attributed to random, syndiotactic structures of PMMA, respectively. The ratio of the two spatial configurations of the PMMA blocks is calculated to be 0.37 : 0.63 according to the integrated intensities of corresponding peaks. Moreover, the resonance of isotactic corresponding can hardly be observed in the spectra which should be at 1.11 ppm.

The kinetic analysis of ATRP was shown in Figure 6, from which we can see that the polymerization kinetics for synthesis of PLLA-*b*-PMMA initiated by trichloro-terminated polylactide is not linear, demonstrating that the living nature of the polymerization is not significant enough. The reason of this has been considered to be the unavoidable oxidation due to air unintentionally introduced during sample harvesting,[24] however, it may most likely results from effects of the DMSO that was used as solvent in the ATRP of MMA at 80°C.[43] The conversion is rather low compared with that of ATRP initiated by low-molecular weight initiator, as a result of the high molecular weight of the macroinitiator, which would induce that active trichloro-end-groups were embedded with the process of reaction. The effect of the molecular weight of the macroinitiator should be further studied in subsequent reports.

Crystallinity and thermal stability of block copolymers

The introduction of PMMA block would disrupt the regularity of chain arrangement of PLLA, thereby

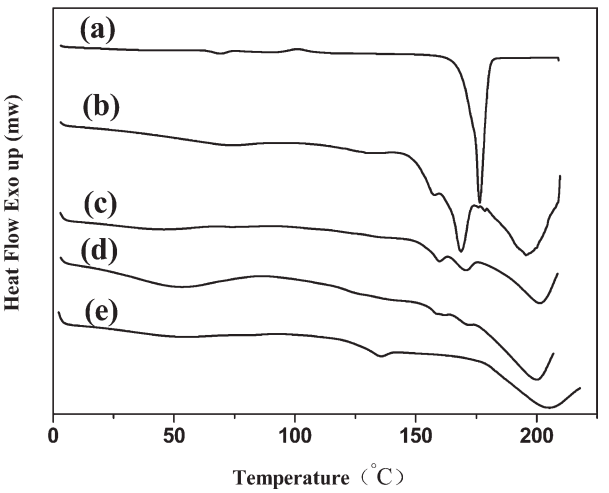


Figure 7 DSC first heating scans of (a) PLLA-Cl, **I2**, and (b–d) PLLA-*b*-PMMA copolymers (b) **B1,** (c) **B2,** (d) **B3**, and (e) PMMA, **M5**.

reducing the crystallinity and abating the brittleness. As shown during the first heating scans of DSC analysis (Fig. 7), the crystalline PLLA macroinitiator exhibits a distinct single melting peak at 176°C, while double melting peaks appear at 158°C, 169°C and gradually become unconspicuous with the PMMA segment increasing. This results from the introduction of PMMA block, which leads to the partial melting and recrystallization of the crystallite during the process of thermal scanning. DSC scans in Figure 8 are the second heating scans, from which we can see that the heating trance of the macroinitiator exhibits a distinct single melting peak at 176°C, and a recrystallization peak at 99°C, but this can not be observed during the second heating scans of copolymer samples. The results demonstrate that

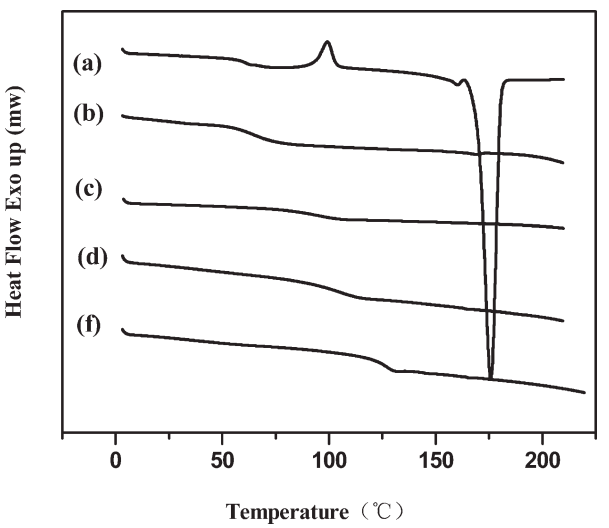


Figure 8 DSC second heating scans of (a) PLLA-Cl, **I2**, and (b–d) PLLA-*b*-PMMA copolymers (b) **B1,** (c) **B2,** (d) **B3**, and (e) PMMA, **M5**.

TABLE III
Glass Transition Temperature of Polymers from the Second DSC Heating Scans

Polymer	Symbol	T_g (°C)
$PLLA_{161}$-Cl	**I2**	64.6
$PLLA_{161}$-*b*-$PMMA_{336}$	**B1**	66.8
$PLLA_{161}$-*b*-$PMMA_{878}$	**B2**	93.5
$PLLA_{161}$-*b*-$PMMA_{1108}$	**B3**	103.3
$PMMA_{605}$	**M5**	120.7

copolymers failed to crystallize under the experiment conditions. Further more, there is only one glass transition temperatures T_g for copolymers in the second heating run, and it rose gradually with increasing PMMA segment, as shown in Table III. XRD results (Fig. 9) also prove that the PMMA chains lead to the decrease of the crystallization of PLLA. For example, the starting polylactide, **I2**, having crystallinity degree of 36, gave the block copolymer, **B1**, which is calculated to have crystallinity degree of 22.

Polylactide is a representative biodegradable polyester with the molecular chain containing many ester groups, which is sensitive to water and heat, and prone to hydrolysis reaction. The thermal stability of PMMA is superior to polylactide, so the thermal stability of block copolymers will be greatly improved comparing with pure polylactide as we can see in Figure 10. For instance, though the first initiating decomposition temperature of the copolymer (175°C), which could be interpreted as the chain terminal decomposition of PMMA (segment), appeared earlier than that of the pure PLLA (265°C), the temperature at maximum weight loss (391°C) is much higher than that of the pure PLLA (306°C)

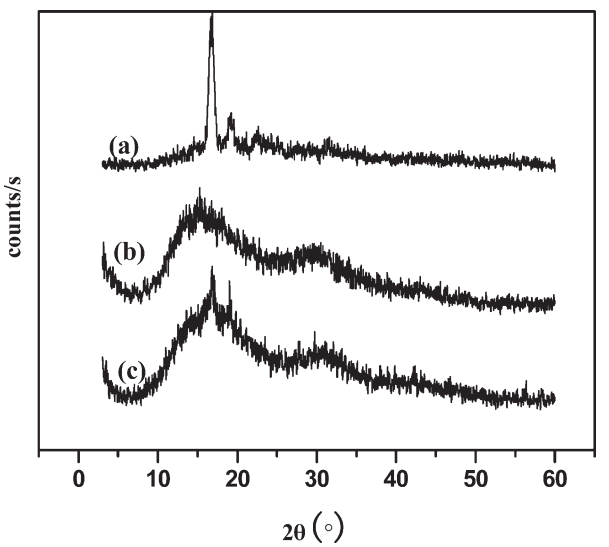


Figure 9 X-ray diffraction patterns of (a) PLLA-Cl, **I4**, (b) PMMA, **M5**, and (c) PLLA-*b*-PMMA, **B1**.

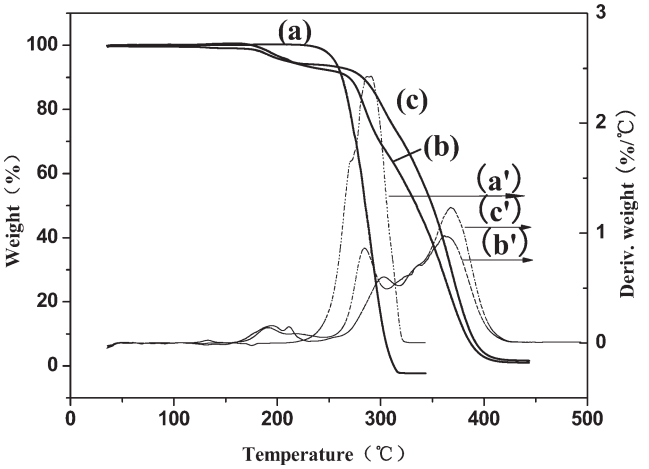


Figure 10 Thermal gravimetric curves of (a) PLLA-Cl, **I1**, (b) PMMA, **M5**, and (c) PLLA-*b*-PMMA copolymer, **B3**.

having the equivalent number average molecular weight. The differential thermogravimetric curves (**a′**, **b′**, **c′**) also demonstrate that thermal stability of copolymers are enhanced comparing with that of not only PLLA but also PMMA.

CONCLUSIONS

The results of the ring-opening polymerization of lactide indicate that, to obtain higher molecular weight and lower molecular-weight dispersity, the desiccation to remove residual moisture in the system is necessary. The 2,2,2-trichloroethanol can be used as the initiator of the ring-opening polymerization of lactide to introduce chlorine atoms at the end of polylactide and further to make polylactide as a macroinitiator for ATRP of other vinyl monomers. Chloro-end-capped macroinitiator PLLA-Cl can successfully initiate the atom transfer radical polymerization of methyl methacrylate using CuCl/PMDETA catalyst system. With the introduction of PMMA segment, the crystallization of PLLA can be inhibited and the thermal performance can be improved. Future work will describe the extension of the monomers and multiblock copolymers, as well as the effect of the molecular weight of the macroinitiator in the process.

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